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ASSESSMENT AND DEVELOPMENT PLAN FOR MONITORING OF ORGANICS IN STORM FLOWS

Allen Molvar, et al

Raytheon Company

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Sewer line scouring, urban runoff, and combined sewage associated with storm events represent a substantial organic pollution load. Since storms usually exhibit high flow rates over a short period of time, the treatment facilities become overloaded and deliver an organic pollution load to receiving water bodies. Many times a significant amount of the combined sewage bypasses the treatment plant and is discharged untreated.

A method for assessing the organic content of storm related wastewaters would permit programming discharges, and monitoring and controlling treatment processes. A variety of laboratory techniques have been employed to measure this organic loading, but only an on-line technique such as continuous TOC will provide the necessary information on a real or quick-time basis.

Experience with currently available commercial TOC units has not resulted in a sense of confidence in the hardware. An evaluation of the instrumentation necessary for a reliable TOC in the stormwater environment leads to the selection of a measurement system based on total combustion of sewage and detection of CO_2 by infrared methods. Tests are presently under way to establish sample processing, modifications of the engineering model, and accumulation of the continuous monitoring data on total organic carbon content of storm and combined sewage.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Combined sewers	*Waste water analysis	13B
*Continuous sampling	*Total organic carbon analyzer	
Control equipment	Automatic control	
Infrared detectors	Organic waste	
Adjusting	Combustion chamber	
Waste treatment	Combined sewage	
	*Storm water environment	

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ASSESSMENT AND DEVELOPMENT PLAN FOR MONITORING OF ORGANICS IN STORM FLOWS

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Contract No. 68-03-0262
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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

An evaluation of existing automatic monitoring devices for measuring organics in sewage was conducted with the objective of developing a reliable system for operation under storm and combined sewer conditions. The study described here is a state-of-the-art report based on the above findings.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

ABSTRACT

Sewer line scouring, urban runoff, and combined sewage associated with storm events represent a substantial organic pollution load. Since storms usually exhibit high flow rates over a short period of time, the treatment facilities become overloaded and deliver an organic pollution load to receiving water bodies. Many times a significant amount of the combined sewage bypasses the treatment plant and is discharged untreated.

A method for assessing the organic content of storm related wastewaters would permit programming discharges, and monitoring and controlling treatment processes. A variety of laboratory techniques have been employed to measure this organic loading, but only an on-line technique such as continuous TOC will provide the necessary information on a real or quick-time basis.

Experience with currently available commercial TOC units has not resulted in a sense of confidence in the hardware. An evaluation of the instrumentation necessary for a reliable TOC in the stormwater environment leads to the selection of a measurement system based on total combustion of sewage and detection of CO_2 by infrared methods. Tests are presently under way to establish sample processing, modifications of the engineering model, and accumulation of the continuous monitoring data on total organic carbon content of storm and combined sewage.

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We feel a deep sense of gratitude to Mr. Anthony Ventatuolo and his staff of the Cranston Municipal Treatment Plant for providing us with the facilities and assistance to obtain sewage samples and conduct the experimental work necessary to establish the accuracy and repeatability of our data.

SECTION I

CONCLUSIONS

1) High solids, surging flows, and adverse environmental conditions associated with storm related wastewaters impose difficult service requirements on automatic rapid organic monitoring systems.

2) Among the various methods of determining organic pollution levels, continuous on-line TOC analysis using the well-known technology of total oxidation and infrared detection of the CO_2 appears to be a "best" analytical choice.

3) The selection and delivery of representative samples containing substantial suspended solids are expected to result from current design and experimental work in this laboratory and by Dr. Philip E. Shelley of Hydrospace Research Corporation.

   Because up to 80 percent of the organic content of stormwater is caused by suspended solids, any meaningful stormwater organic monitoring system must take a representative sample from the main flow, suitably transport and analyze it without the loss of any suspended solids.

4) At this time, no commercially available rapid on-line automatic organic monitoring system is suitable for stormwater service. However, the authors believe that most of the components to build such a system are available from appropriate suppliers. But several essential components such as sample transporting and conditioning equipment and combustion reactors must be fabricated especially for stormwater duty.

5) To be successful, the organic monitoring system must be capable of unattended operation; moreover, the service requirements should be within the capability of a typical municipal maintenance staff.

SECTION II

RECOMMENDATIONS

1) After a decade of laboratory TOC and TOD analyses, the concept and utility of rapid organic monitoring clearly has been demonstrated. The transition from the laboratory (batch) type to a continuous on-line instrument involves the fabrication of a rugged, reliable instrument equipped with suitable alarms and fail safe modes. The need for mechanical ruggedization cannot be overstressed. Accordingly, an engineering model should be fabricated with commercially available (whenever possible) and custom made components. The feasibility of representative solids conditioning and transport, along with the accumulation of accuracy, precision, response time, drift and reliability data should be determined via stormwater simulations.

2) Published stormwater characterization data indicate that a mixture of raw sewage and settled primary sludge should simulate stormwater, especially the first flush. During this laboratory study (to be conducted at Cranston, RI STP), the alarm functions, and startup and shutdown procedure can be verified in the field. An interim report will describe this phase of the study and assess the desirability of continuing this project.

3) After demonstrating the feasibility of the engineering model, the developed system should be ruggedized, and automated for subsequent field tests under actual storm conditions. An important aspect of these field tests involves assessing the ability of a well run municipality to operate and maintain the stormwater organic monitoring system. Arrangements have been made to test this system at Boston University Stormwater Detection and Chlorination Station. During the field tests, a series of automated grab and/or composite samples will be taken for TOC, and BOD analysis via standard EPA approved laboratory methods.

SECTION III

INTRODUCTION

The United States Environmental Protection Agency's (EPA) Storm and Combined Sewer Pollution Control Research and Development Program developed three storm-event strategies other than separation: control, treatment, and combinations of these two. Briefly, successful treatment and control of stormwater and combined sewage depends heavily on the ability to measure pollution loads and subsequent removal efficiencies. Consider, for example, stormwater storage utilizing the combined sewer's inherent capacity. If the storm is severe, the storage demand will exceed available capacity and the excess combined sewage must overflow to the receiving water. Based on the strengths of the incoming combined sewage, the least polluted stormwater can be discharged into the stream. Without any measurements of organic strength, no rational method exists for selecting or programming overflows. The organic load (product of flow rate and Total Organic Carbon concentration) represents a significant pollutant parameter since organic material exerts an oxygen demand on the receiving system.

Transient flow rate monitoring over large ranges is a difficult problem but previous efforts and demonstrations clearly indicate that stormwater and combined sewage flow rate monitoring is addressable by well established instruments. Although several Total Organic Carbon, Total Oxygen Demand or COD analyzers are commercially available, no existing system for automatic monitoring of organics

in stormflow has been successfully demonstrated to automatically analyze storm and combined sewage samples. Since storm events lead to rapidly changing wastewater concentration profiles with the occurrence of very high suspended solids levels, a dedicated organic monitoring system must be specifically designed for this service; satisfactory commercial components, however, should be employed, when available, so as to keep the project cost to an absolute minimum. Recognizing the need for a suitable organic monitoring instrument, EPA awarded Raytheon's Environmental Systems Center a contract to develop a rapid on-line Automatic Monitoring System to measure the organic content of storm and combined sewage.

Because laboratory researchers have investigated wastewater total organic carbon (TOC) determination for the last five years, the technical literature contains a significant amount of relevant information. The Assessment and Development Plan presented herein, evaluates the suitability of reported technology, equipment, and devices with respect to storm and combined sewage TOC monitoring. Moreover, pertinent user-experience and comments are presented to give insight into the operational requirements. From an examination of stormwater and combined sewage characteristics, a rational set of automatic organic monitoring component specifications were generated to insure acceptable performance of the developed system in the storm environment. The commercially unavailable components or unacceptable devices are clearly identified and Raytheon's experiences, with supporting data, have been brought to bear in developing the needed components. This report also discusses the development tasks and laboratory testing program leading to the construction and verification of rapid, reliable, continuous storm and combined sewage organic monitoring. After successful laboratory demonstration, Phase 1, a ruggedized, automated analyzer will be thoroughly field tested in MDC's Boston University Stormwater Detention and Chlorination Station. In short, this Assessment and Development Plan Report summarizes the findings of a comprehensive study

of previous TOC investigations, and existing important components and devices; moreover, it presents a clear cut, action plan with accompanying schedules leading to development of a storm and combined sewage automatic organic monitoring system.

SECTION IV

STORM AND COMBINED SEWAGE CHARACTERISTICS

To develop an automatic, on-line organic monitoring instrument, the designers must be thoroughly acquainted with the characteristics of the intended samples—storm water and combined sewage. Human factors (i.e., maintenance capabilities), environmental conditions, and operational modes must also be considered during the instrument design phases. Consequently, a brief description of storm events and subsequent storm and combined sewage temporal variations follows.

Most of the 1,300 sewered communities in the United States are served by combined sewers; a much smaller number have segregated facilities where storm water is transported in a separate sewer. Although storm events only occur 4 to 5 percent of the time, untreated overflows from combined sewers and storm water are a substantial source of water pollution. For example several studies[1, 2] demonstrated that annual Biochemical Oxygen Demand (BOD) contributions from storm-related wastewaters are approximately equal to the BOD load of secondary treated sanitary effluent.

Because of the random nature of rainfall events, the quantity of collected runoff changes continuously; but the integrating effects of the drainage, infiltration, collection, depression storage, gutter-flow and sewer-flow routing processes, produce relatively smooth hydrographs as illustrated in Figure 1. With respect to flow-rate properties, storms can be classified as either long or short duration and high or low intensity.

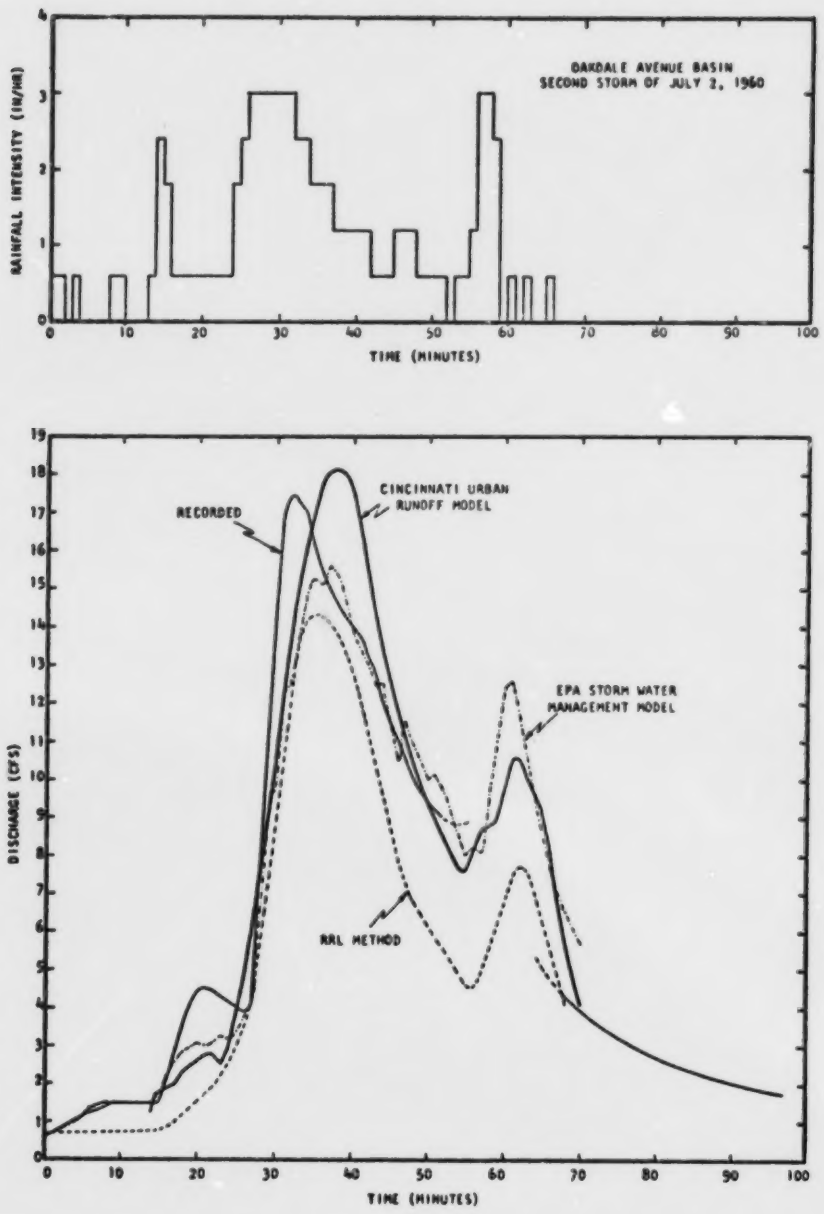


Figure 1. Rainfall hyetograph, calculated and observed runoff hydrographs, Oakdale Avenue Basin, Chicago, second storm of July 2, 1960 (Source: Urban Runoff Characteristics, EPA, Water Quality Office, October 1970, p. 275.)

Stormwater and combined sewage quality parameters vary from storm to storm, and also change rapidly during storm events. Frequency of changes in sewage quality depends upon rainfall intensity, duration, antecedent conditions, land use, topography, flush characteristics and other factors. Temporal variation data, Figure 2, clearly indicate that the organic concentration changes vary rapidly with respect to time. Notwithstanding that there is no apt description of "typical" combined sewage, it is informative to examine the general properties of storm and combined sewage. Because of poor flow characteristics of combined sewers during dry weather, settled solids build up in the combined sewer. When a storm occurs, the greatly increased flow scours the collection system and causes the "first flush" phenomenon with suspended solids concentrations frequently reaching 1,700 mg/l. In addition as the storm run-off drains from urban land areas, it picks up accumulated debris. Tables 1 and 2 display concentration ranges usually encountered in combined sewer overflows and urban stormwater run-off, respectively. The organic concentration, as measured by either BOD or Chemical Oxygen Demand (COD), varies over a large range of values; it is estimated that the Total Organic Carbon (TOC) ranges from 10 to 1000 mg/l.

Since stormwater and combined sewage contains an appreciable amount of suspended organic matter, any meaningful, total-organic analyzer must measure the organic contribution of the suspended solids. The particle-size distributions and density properties of the suspended matter become important parameters with regard to sample-taking, transporting and conditioning. One study[3], related to fixed screening, presents particle-size-distribution data (Table 3) that indicate the bulk of the suspended organics are less than 1.0 mm in diameter. In general, the further downstream collection points are (i.e., closer to the end of the delivery system), the smaller the particle sizes are, since transporting under storm conditions usually breaks up the larger organic solids. Moreover,

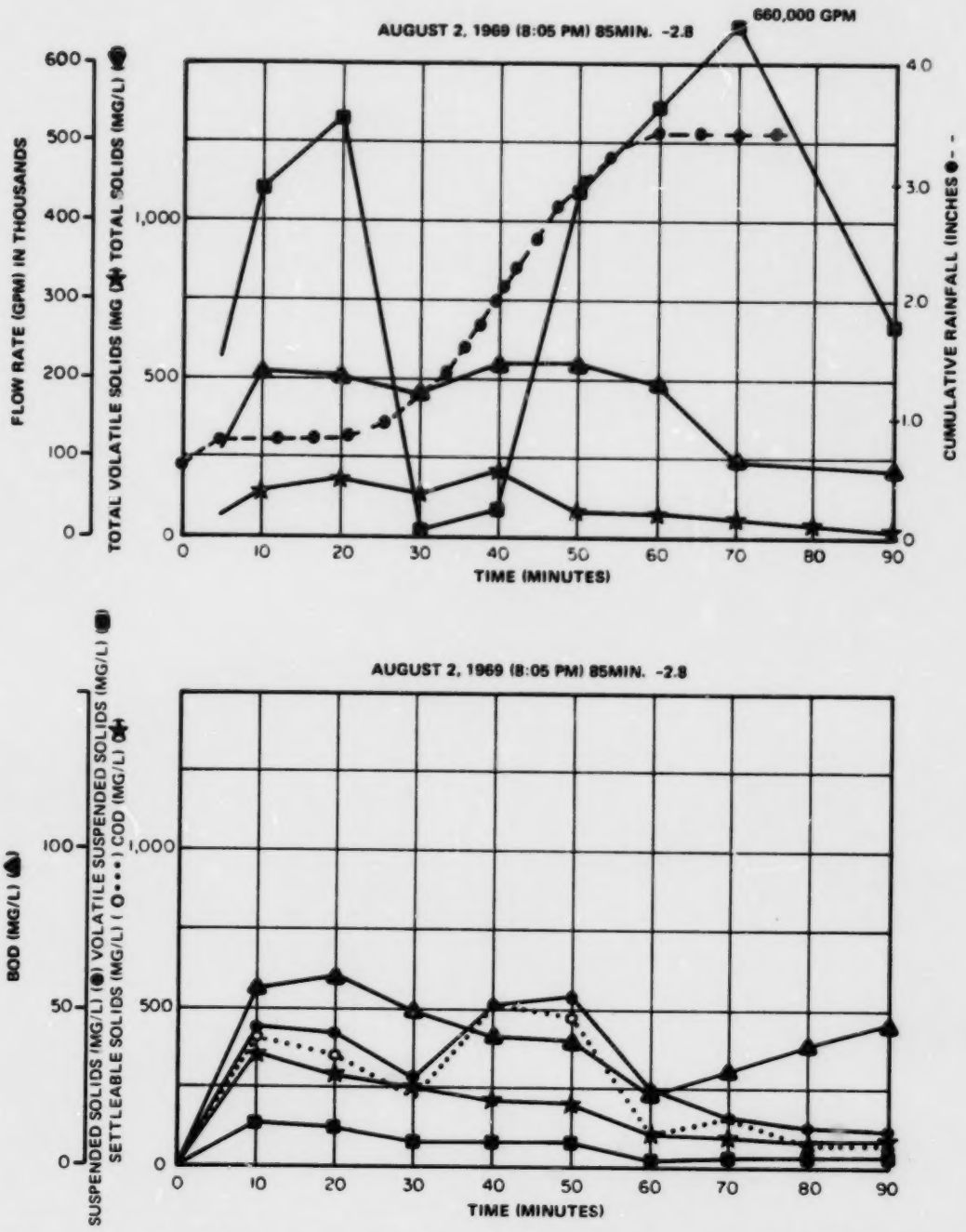


Figure 2. Long, intense storm in Combined Sewer District G-4 (gpm x 0.0631= 1/sec; in. x 2.54 = cm) (Reference: "Journal of Water Control Federation," Vol. 43, p. 2041, October 1971.)

Table 1. CHARACTERISTICS OF COMBINED SEWER OVERFLOW*

Characteristic	Range of Values
BOD_5 (mg/l)	30—600
TSS (mg/l)	20—1,700
TS (mg/l)	150—2,300
Volatile TS (mg/l)	15—820
pH	4.9—8.7
Settleable solids (ml/l)	2—1,550
Organic N (mg/l)	1.5—33.1
NH_3N (mg/l)	0.1—12.5
Soluble PO_4 (mg/l)	0.1—6.2
Total coliforms (no./100 ml)	20,000—90 x 10^6
Fecal coliforms (no./100 ml)	20,000—17 x 10^6
Fecal streptococci (no./100 ml)	20,000—2 x 10^6

*Selected data.

Table 2. CHARACTERISTICS OF URBAN STORMWATER*

Characteristic	Range of Values
BOD_5 (mg/l)	1—>700
COD (mg/l)	5—3,100
TSS (mg/l)	2—11,300
TS (mg/l)	450—14,600
Volatile TS (mg/l)	12—1,600
Settleable solids (mg/l)	0.5—5,400
Organic N (mg/l)	0.1—16
NH_3N (mg/l)	0.1—2.5
Soluble PO_4 (mg/l)	0.1—10
Total PO_4 (mg/l)	0.1—125
Chlorides (mg/l)	2—25,000†
Oils (mg/l)	0—110
Phenols (mg/l)	0—0.2
Lead (mg/l)	0—1.9
Total coliforms (no./100 ml)	200—146 x 10^6
Fecal coliforms (no./100 ml)	55—112 x 10^6
Fecal streptococci (no./100 ml)	200—1.2 x 10^6

*Selected data.
†With highway deicing.

Table 3. CHARACTERISTICS OF COMBINED SEWAGE BULK SAMPLE

5 November 1969					
Time	0520	0620	0720	0820	0920
Flow, cfs	0.591	0.711	0.706	0.499	0.075
Total Solids, mg/l	148	140	180	220	432
Total Volatile Solids, mg/l	40	44	64	112	224
Total Suspended Solids, mg/l	34	45	63	57	185
Total Volatile Suspended Solids, mg/l	15	31	24	40	131
Settleable Solids, ml/l	5	0.7	1	0.6	0.7
Floatables, mg/l	1.4	2.4	3.9	2.3	11.8
Particle Size Distribution, mg/l					
>3.327 mm	0	trace	trace	14.4	29.5
3.327-0.991 mm	0	trace	trace	11.2	14.3
0.991-0.295 mm	trace	trace	5.5	42.5	36.5
0.295-0.074 mm	trace	4.1	5.6	22.9	33.4
<0.074 mm	16.3	18.4	34.5	69.5	135.7
size at 50-percentile by weight, mm	-	-	0.018	0.14	0.05
BOD, mg/l	9.5	11.0	11	61	175
COD, mg/l	51.6	62.5	82.5	132.4	626
Hexane Extractable Material, mg/l	4.1	4	3.8	7.2	14.5
Total Coliforms, MPN/100 ml	2.3×10^5	2.3×10^5	3×10^4	4.3×10^6	2.3×10^6
Fecal Coliforms, MPN/100 ml	3×10^4	3×10^4	3×10^4	4.3×10^6	9×10^5
Fecal Streptococci, MPN/100 ml	9×10^3	4.3×10^4	9×10^3	4.3×10^5	3×10^4

19 December 1969					
Time	1045	1145	1240	1340	1440
Flow, cfs	0.375	0.447	0.413	0.073	0.046
Total Solids, mg/l	95	115	135	415	275
Total Volatile Solids, mg/l	50	65	60	180	125
Total Suspended Solids, mg/l	19	46	31	112	84
Total Volatile Suspended Solids, mg/l	9	31	21	70	55
Settleable Solids, ml/l	0.2	1.5	1	3.5	2.5
Floatables, mg/l	7.1	3.6	4.2	4.4	3.9
Particle Size Distribution, mg/l					
>3.327 mm	0	0	0	56.9	6.3
3.327-0.991 mm	0	1.7	4.8	5.1	4
0.991-0.295 mm	2.9	4.2	11.6	16.3	8.9
0.295-0.074 mm	5.3	12.5	11.8	27.7	24.6
<0.074 mm	10.8	27.6	2.8	6	44.2
size at 50-percentile by weight, mm	0.054	0.049	0.34	0.45	0.074
BOD, mg/l	14.7	15	16.8	77.4	40.5
COD, mg/l	76.8	57.6	57.6	221	144
Hexane Extractable Material, mg/l	4.1	6.1	4.8	36.3	1.6
Total Coliforms, MPN/100 ml	1.5×10^5	4.6×10^6	4.6×10^6	2.4×10^6	4.6×10^6
Fecal Coliforms, MPN/100 ml	9.3×10^4	4.3×10^5	2.4×10^6	4.6×10^5	4.6×10^5
Fecal Streptococci, MPN/100 ml	7.5×10^3	4.3×10^3	2.3×10^3	1.1×10^5	$>1.1 \times 10^5$

Table 3. CHARACTERISTICS OF COMBINED SEWAGE BULK SAMPLE (cont)

21 December 1969					
Time	930	1025	1125	1225	1410
Flow, cfs	0.910	0.175	0.169	0.105	0.070
Total Solids, mg/l	110	280	210	250	400
Total Volatile Solids, mg/l	80	165	115	140	140
Total Suspended Solids, mg/l	55	89	79	98	118
Total Volatile Suspended Solids, mg/l	42	76	64	68	94
Settleable Solids, ml/l	2.5	13	4.5	2.5	7
Floatables, mg/l	2.3	1.5	3.6	3.5	4.2
Particle Size Distribution, mg/l					
>3.327 mm	8.8	0	0	0	0
3.327-0.991 mm	14.1	8.6	5.9	20.2	8.3
0.991-0.295 mm	9	32.4	13.0	16.3	34.7
0.295-0.074 mm	15.1	18.1	14.7	25.8	19.5
<0.074 mm	8	29.9	45.4	35.7	50.7
size at 50-percentile by weight, mm	0.54	0.22	0.047	0.15	0.11
BOD, mg/l	32.6	75.9	56.4	62.4	102
COD, mg/l	86.4	158	182	154	257
Hexane Extractable Material, mg/l	4.4	2.5	5.1	6.7	28.5
Total Coliforms, MPN/100 ml	4.6×10^5	2.4×10^6	2.4×10^6	9.3×10^5	4.6×10^6
Fecal Coliforms, MPN/100 ml	4.3×10^4	2.4×10^6	2.4×10^6	4.6×10^5	4.6×10^6
Fecal Streptococci, MPN/100 ml	9.1×10^2	-	-	-	2.4×10^4

20 January 1970					
Time	1625	1725	1835	1930	2030
Flow, cfs	1.05	0.605	0.894	0.431	0.556
Total Solids, mg/l	84	84	184	148	60
Total Volatile Solids, mg/l	48	16	68	72	36
Total Suspended Solids, mg/l	29	30	15	33	17
Total Volatile Suspended Solids, mg/l	19	23	14	28	16
Settleable Solids, ml/l	0.2	1.2	0.2	0.2	0.6
Floatables, mg/l	4.2	22.3	3.9	4.7	2.8
Particle Size Distribution, mg/l					
>3.327 mm	0	0	0	0	0
3.327-0.991 mm	0.5	1.6	1.3	2.6	0.9
0.991-0.295 mm	2.1	5.7	2.6	2	1.5
0.295-0.074 mm	6.2	5.1	4	4.2	4.8
<0.074 mm	10.2	17.6	7.1	25.2	9.8
size at 50-percentile by weight, mm	0.065	0.036	0.084	0.01	0.055
BOD, mg/l	21.2	18.2	7.97	30.4	12.7
COD, mg/l	72	127	311	349	43
Hexane Extractable Material, mg/l	2	44	3.8	10.4	5
Total Coliforms, MPN/100 ml	3×10^4	3.6×10^4	7.3×10^4	3.6×10^4	3.6×10^4
Fecal Coliforms, MPN/100 ml	$< 3 \times 10^4$	3.6×10^4	7.3×10^4	3.6×10^4	3.6×10^4
Fecal Streptococci, MPN/100 ml	2.3×10^4	2.3×10^4	9.1×10^3	3.6×10^3	7.3×10^3

Table 3. CHARACTERISTICS OF COMBINED SEWAGE BULK SAMPLE (cont)

27 January 1970					
Time	0130	0230	0345	0430	0530
Flow, cfs	1.23	0.603	0.176	0.058	0.039
Total Solids, mg/l	95	60	73	72	90
Total Volatile Solids, mg/l	55	32	40	37	43
Total Suspended Solids, mg/l	8	4	6	6	6
Total Volatile Suspended Solids, mg/l	7.5	4	6	5	6
Settleable Solids, ml/l	0.3	0.1	0.2	0.05	0.05
Floatables, mg/l	1.4	1	0.8	0.6	0.9
Particle Size Distribution, mg/l					
>3.327 mm	0	0	0	0	0
3.327-0.991 mm	1.4	0.2	0.2	0.3	2
0.991-0.295 mm	3.7	0.9	1.7	0.5	1.1
0.295-0.074 mm	9.6	2.4	5.5	1.9	1.9
<0.074 mm	12.9	7	3.9	7.9	8
size at 50-percentile by weight, mm	0.082	0.035	0.11	0.023	0.028
BOD, mg/l	3.3	<1.5	4.65	1.95	17.7
COD, mg/l	64	16.9	31	31	52.5
Hexane Extractable Material, mg/l	3.2	3.8	2.6	2	5.4
Total Coliforms, MPN/100 ml	2.3×10^{6}	9×10^{5}	9×10^{5}	4.3×10^{6}	7×10^{5}
Fecal Coliforms, MPN/100 ml	4×10^{4}	$<3\times10^{3}$	$<3\times10^{5}$	$<3\times10^{5}$	$<3\times10^{5}$
Fecal Streptococci, MPN/100 ml	2.3×10^{4}	4.3×10^{4}	4×10^{3}	2.4×10^{6}	1.5×10^{5}

13 February 1970					
Time	0645	0745	0845	0945	1045
Flow, cfs	1.069	0.199	0.1024	0.0932	0.079
Total Solids, mg/l	148	152	432	552	348
Total Volatile Solids, mg/l	96	72	316	248	156
Total Suspended Solids, mg/l	49	50	127	95	115
Total Volatile Suspended Solids, mg/l	29.5	33	115	80	94
Settleable Solids, ml/l	0.6	2.5	11.5	4	14
Floatables, mg/l	4.65	1.83	3.68	3.36	1.73
Particle Size Distribution, mg/l					
>3.327 mm	0	0	34.2	126	0
3.327-0.991 mm	9.4	11.6	9.8	56	29
0.991-0.295 mm	10.6	24.2	28	47	18
0.295-0.074 mm	42.2	3.4	22.6	43	16
<0.074 mm	33.4	2.6	12.4	78	62
size at 50-percentile by weight, mm	0.116	0.64	0.64	1.12	0.076
BOD, mg/l	21	55.8	139.1	168	121.4
COD, mg/l	88.4	176.8	353.6	402.2	371.3
Hexane Extractable Material, mg/l	12	7.7	20.2	44.1	21.5
Total Coliforms, MPN/100 ml	1.1×10^{7}	2.4×10^{6}	2.4×10^{6}	$>1.1\times10^{7}$	1.1×10^{7}
Fecal Coliforms, MPN/100 ml	9×10^{4}	4.3×10^{5}	2.4×10^{6}	$>1.1\times10^{7}$	9.3×10^{5}
Fecal Streptococci, MPN/100 ml	4.3×10^{4}	4.6×10^{5}	2.4×10^{5}	4.6×10^{5}	9.3×10^{4}

most storm and combined sewage exhibit stratified flow properties, where the grit, sand and other dense particulate material are concentrated near the bottom of the conduit. It is reasonable to assume that these lower areas contain mostly inorganic grit and that the bulk of solid organics is collodial, super collodial or suspended particles less than approximately 1.0—10 mm in diameter. Although floatable materials such as boards, paper, and other large debris may contain organic compounds, they can not be considered as part of the analyzer-sample universe for obvious reasons.

SECTION V

TECHNICAL LITERATURE RELATED TO AUTOMATIC ORGANIC MONITORING DEVICES

In the last five years, an increased awareness of the problems of environmental pollution motivated research into more effective measuring and monitoring methods. One of the problems considered has been Total Organic Carbon (TOC) determination, because the delivery of unsuitably treated organic wastes, industrial and municipal, to receiving waters has resulted in eutrification of our water resources.

BOD (Biological Oxygen Demand)

In order to prevent the discharge of unsuitably-treated sewage, a number of indices has evolved which provides information about the organic content of sewage. Historically, the Biochemical Oxygen Demand (BOD) was the first test devised to measure the organic concentration of waste waters. The BOD test, however, has two severe shortcomings: poor precision (± 18%) and requirement of five days to complete. Unacclimated seed bacteria, toxicants and human errors are the major factors which cause this poor precision. Because five days are required to complete a BOD test, this procedure can only supply historical data.

RESPIROMETRY

Inasmuch as control techniques require real-time data for implementation of corrective actions, several researchers addressed themselves to developing a rapid BOD technique,[4, 5, 6] commonly referred to as respirometry. Instead of measuring the

oxygen depletion after five days, they monitored the oxygen uptake rate during a 15-minute to 1-hour interval; the uptake rate is used to predict the 5 BOD through a predetermined estimation coefficient. Although respirometers work reasonably well in the laboratory, on-line versions are usually very unreliable. Moreover, respirometers exhibit a poorer precision than the BOD test, and are also vulnerable to the same interferences.

COD (Chemical Oxygen Demand)

Because of the inherent limitations of biological techniques, a more rapid, reliable test was necessary to measure organic pollution. Liquid-phase oxidation of organics by acidulated chromate was developed to monitor the organic concentration of waste waters; this reaction, carried out under reflux conditions, requires two hours for completion. As the reaction proceeds, the reduction of the chromate to trivalent chromium can be seen colorimetrically. This measurement, expressed as Chemical Oxygen Demand (COD), has been modified by several researchers [7] to reduce the reaction time to 15 minutes. Because COD determinations require consumable reagents, and high temperatures, all COD procedures need constant attention by skilled technicians. Although use of an Autoanalyzer [8] can speed the data delivery, it still requires a regular supply of reagents and inspection by skilled personnel.

Since one of the reaction products of chromate oxidation is carbon dioxide, instruments have been designed which monitor the carbon dioxide conductometrically. [9] These devices, which display their results as Total Organic Carbon (TOC), have most of the problems of COD. While inorganic reducing agents do not oxidize to CO_2, neither do a number of organics. [7] Despite the improvement in organic estimation, all automated COD procedures are too slow and not suitable for unattended operation.

TOC (Total Organic Carbon)

Vapor-phase oxidation of waste in water (950°C) was developed[10] for the purpose of providing a complete, rapid determination of the carbon content (TC). Acidifying the sample and purging with CO_2 free gases, removes the inorganic carbonates; then this combustion technique measures the total organic concentration. This procedure has been used to measure Total Organic Carbon in a number of locations,[11] and has been found to give useful rapid data.

Several investigators attempted to correlate BOD and COD data to corresponding TOC values. As expected, BOD correlations suffered from the shortcomings inherent in the BOD test. COD and TOC, however, correlate well.[12, 13]

The earliest forms of the Total Organic Carbon instrumentation used non-dispersive infrared (NDIR) detection of CO_2 concentration in the gas stream. In one case CO_2 was reacted over a platinum catalyst to produce CO[14] which was also monitored by NDIR. While there may be some place where the measurement of CO offers some advantage, it has not found great acceptance to date; CO_2 has been preferred.

In choosing a means for the measurement of carbon, it is desirable and (for the purposes of reliable instrumentation) necessary to minimize the complication of the system. For this reason, NDIR lends itself to considerable economy of design and has found the most common acceptance.

Flame ionization detectors (FID) are highly sensitive and linear devices, requiring the CO_2 formed during combustion to be catalytically converted to methane.[15] This reaction needs hydrogen. Moreover, a flame is necessary to provide the ionization and a complex array of electronics is required to develop output signals. If one neglects the conversion of the carbon to methane, the bonding of the hydrocarbon becomes a large factor in the FID signal.[16] In

spite of this excessive complication, considerable effort has been spent on this approach.[17] A recent survey of user experiences (Table 4) found FID techniques unreliable in field environments.

Alternative CO_2 detection techniques have also been investigated. A differential conductivity approach has been used by H. Wosthoff.[9] Because of the need for calibrated solutions and flow-controlled conditions, differential conductivity measurements become complicated.

Rather than measure the amount of CO_2 formed during combustion, some investigators have measured the oxygen consumed to form CO_2; unfortunately, the electrochemical oxygen sensors tend to be unreliable and susceptible to contamination. They are usually temperature sensitive and require considerable maintenance of the conducting media which is susceptible to contamination. For wastewater oxidation, only a small amount of oxygen is consumed out of a high background concentration; the TOD determinations are calculated by the difference between input and output concentration with the resultant summation of error. Accordingly, history of devices of this type is frequently associated with unreliable results.

It has been reported that dissolved organics can be detected by ultraviolet (UV) absorbence[18] but the high organic content of the suspended solids (particulate matter), would both absorb and disperse UV. Bond breaking occurs under the influence of UV as does polymerization which is likely to form UV absorbing films in the system. Consequently for stormwater sample, this approach becomes inappropriate and cannot be considered as an alternative method for monitoring the storm-related organics.

Although TOC instrumentation lends itself to automation (because of fast oxidation and reliable detection), on-line continuous TOC analyzers experienced a number of difficulties. One of the most serious is that samples containing suspended solids

Table 4. SELECTED AUTOMATIC ON-LINE USER EXPERIENCE

Organization (User)	Source	Analyzer	Experiences
Dupont Inc.	Mr. R. Coon	Ionics-TOC	Dupont monitors "soluble" influent and effluent TOC in their Waynesboro, Va. activated sludge facility. In spite of their effort to strain and filter the sample, the Ionics TOC analyzer's performance was unacceptable because of frequent sampling valve plugging, and sample flashing difficulties in the combustion reactor. It is estimated that 200 man hours of technician time are required for proper maintenance and calibration.
National Air and Water Research Council	Mr. D. Buckley	Astro-Ecology TOC	In 1972, the National Air and Water Research Council tested an Astro TOC analyzer in their Tufts University Laboratory. Because of excessive noise and drift on KHP Solutions (standard) and on selected Kraft liquors, field evaluations of this instrument were cancelled. Astro corrected the noise problem by electronically filtering the analyzer output signals which increased response time to several hours. Modifications to the reactor volume and sample flow rates were also implemented, but no test results are available.
City of Palo Alto Municipal Wastewater	Mr. R. Doty Mr. R. Niese	Calibrated Instr. Co.	A laboratory evaluation of this TOC analyzer, which employs liquid phase oxidation, on raw sewage, primary clarifier, secondary clarifier and final effluents indicated significant errors (about 20%) due to chloride interference and loss of volatile organics.
		Astro-Ecology TOC	In mid November 1973, an Astro TOC instrument started monitoring the primary effluent which contained about 80 PPM of suspended solids. As of January 2, 1974 no plugging was observed. However, no correlations with regard to other methods of measuring the organic content, have been performed. Results appear encouraging, but performance data are unavailable.
International Paper Mobile, Ala.	Mr. R. Wise EPA	Astro-Ecology	Initially the Astro TOC analyzer failed when operating on primary effluent due to plugging and corrosion problems. After changing the trouble components to Inconel, this analyzer performed without failure. No data is available on accuracy or the suspended solids content of the samples.
Dow Chemical Company Freeport, Texas	Dr. M. Zeitoun	Ionics-TOC	Dow intermittently monitors TC content of their influent wastewater and mixed liquor from their aeration tank. The aeration tank's mixed liquor contains approximately 2500 mg/l of MLVSS; an elaborate batch homogenization system is required to condition the sample prior to analyses. This system has an accuracy of ±8% and requires extensive maintenance every three days.

could not representatively be introduced into the system. Automatic slider valves, and injection valves simply plugged up and became inoperative. In addition, combustion reactors would plug on the refractory components in the sample. Special consideration should be given to insure adequate heat transfer and complete oxidation. Also, most sparging systems necessary to eliminate inorganic carbonates are vulnerable to solids accumulation and plugging. Through careful system design (utilizing known technology), it is anticipated that these problems can be solved.

SECTION VI

EVALUATION OF AVAILABLE AUTOMATIC TOTAL ORGANIC CARBON INSTRUMENTATION

When instruments are introduced to individuals who are involved in analyzing samples, the instruments are generally treated from the sample point of view. The sample is processed through a number of operations that must be controlled in such a way that the instrument will deliver valuable and useful data. One becomes accustomed to this approach as a student and on exposure to instrument salesmen. For the purpose of describing available TOC analyzers, this is a totally acceptable approach.

From the point of view of instrumentation, it is possible to devise a somewhat more efficient approach than the classical one. This pretty much represents the point of view of the instrument designer and the usual experimental approach to engineering the design. The first and perhaps the only independent choice that is possible is a transducer. The transducer is a device where the physical or chemical characteristics of a system are converted to an electrical signal. When an informed and experienced judgment is made about the transducer effect, this choice acts as a constraint on all further choices. The sample processing and the signal processing must be consistent with that initial choice. To demonstrate this approach we have chosen the format in Figure 3.

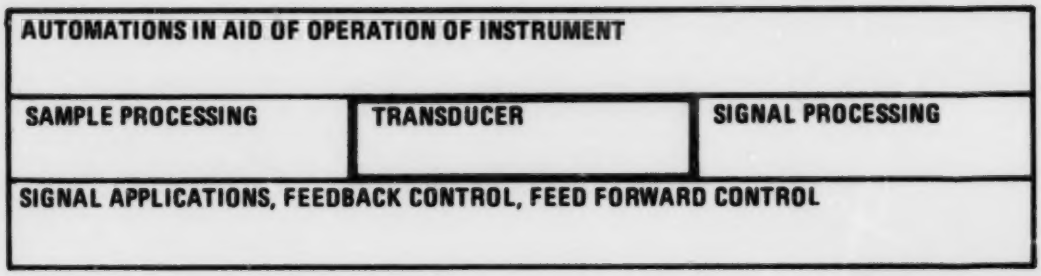


Figure 3. Diagrammatic representation of available TOC instruments

An example would be an appropriate aid to understanding this approach. A careful examination of the various possible and practical alternatives might lead an individual to choose to measure TOC by making an infrared measurement of the CO_2 in the gas stream. It is then necessary that he provide a means for the efficient oxidation of the carbon compounds in sewage and find means of handling the sample and delivery system in a way to bring about an efficient quantitative oxidation. This may be described as material processing.

There are several systems for the measurement of infrared adsorption. Requirements of sensitivity, control and economy of design restrict the choices here. A signal is generated for the purpose of information retrieval. This operation requires signal processing.

To these functions are generally added a variety of automatic control systems which protect the instrument and act as a convenience to the operator.

To aid in the evaluation of available automatic TOC instrumentation, Raytheon devised the following diagrammatic representations (Figures 4 through 7) of the available instruments in order to compare the functions described above. Efforts to obtain detailed information of the several commercially available TOC units has proven to be difficult. Based on the more easily available commercial literature, it is possible to make some comparisons between devices. They are all quite different devices and are much less automated than would normally be expected of devices to be operated continuously on sewage samples. Some of these designs would indicate that they require considerable maintenance.

Figure 4 describes the H. Wostoff device marketed by Calibrated Instruments, Inc. which is a continuous commercial TOC analyzer employing oxidation of the organic carbon by chromate to form CO_2. This is essentially the process employed in the estimation of Chemical Oxygen Demand (COD). The CO_2 evolved

H. WOSTHOFF
Calibrated Instruments, Inc.

AUTOMATION OF OPERATIONS, ALARMS

Zero adjusted with distilled water
Calibration solution of KNa tartrate used to adjust instrument.
Several reagents are consumed at the rate of 1 ml/min and must be supplied frequently.

SAMPLE PROCESSING

Inorganic carbonate and chloride removed by sulfuric acid. The carbon compounds are reacted with acidulated chromate to form CO_2 which is blended with CO_2 free air.

Cooling coils provided for temperature control of effluent.

TRANSDUCER

Differential conductivity cell using NaOH. Monitors the change in conductivity resulting from the absorption of CO_2 by the dilute NaOH solution.
TOC operates in the 0 → 500 mg/l c/range.

SIGNAL PROCESSING

Meter readout.
Two electrode conductivity measurement in which a voltage is applied and the current monitored (J. Searle)

SIGNAL APPLICATIONS, FEEDBACK CONTROL

0 → 20 ma analog signal output for feedback control.
Meter readout.

Commercially available system for the independent determination of TOC and COD
COD (not considered here) is achieved by chromate reduction
Modular design makes it possible to stack operations

Figure 4. Diagrammatic representation of H. Wosthoff TOC

from this process is collected in sodium hydroxide solution and determined by means of differential conductivity.

Figure 5 is a TOC measuring device marketed by Ionics. This device employs Flame Ionization Detection (FID) as a means of determining carbon. A low temperature combustion furnace is provided for the determinatien of inorganic carbon.

The device described in Figure 6 is produced by Enviro-Control. It measures TOD which is indirectly associated with the formation of CO_2. The fluidized bed reactor is reported to be designed so as to accept solids up to 100 microns.

Astro-Ecology Corporation provides an instrument capable of measuring TOC or TOD. This device is described in Figure 7. The Astro-Ecology Corporation Model 1500 uses the MSA Lira as an NDIR to measure CO_2 from a catalytic combustion process.

Our information indicates that these are the only devices commercially available at present for the continuous determination of TOC. It is interesting to note that each of them employs a different transducer effect. A review of user experience will be of interest to estimate the comparative problems and advantages of each transducer choice.

TOC USER EXPERIENCES

Field experiences were sought from automatic, on-line total carbon, and Total Organic Carbon instrument users, who had applications somewhat similar to storm and combined sewage. This criteria, in conjunction with user lists (accumulated from manufacturers and Raytheon's experience in related projects), lead to the selection of the organizations listed in Table 4. These selected users utilized most of the commercially available analyzers in a variety of monitoring tasks.

IONICS MODEL 1224 TOC and TOD

AUTOMATION OF OPERATIONS, ALARMS

Continuous operation option possible, single or multiple grab bed or stream samples are possible. Front panel switch selects TC or TOC option. N_2 + instrumentation must be supplied. Span set on known solutions. High and Low Level Alarms,

SAMPLE PROCESSING

Measures organic and inorganic carbon. Milton Roy H_2 generator supply. Purified air prepared over a catalyst bed. 40 microliter sample injection into a catalytic reactor at 880° C gives CO_2 converted to methane and the methane burned in flame. Inorganic carbon determined independently by low temperature combustion. Additive automatically replenishes acid.

TRANSDUCER

FID linear output
High sensitivity 0 → 50 mg/l
Flame Ionization Detector with high sensitivity in the 0 to 50 mg/l range.

SIGNAL PROCESSING

Apparently analog signal is converted to digital making convenient memory storage and subtraction. Reconversion to graphical output on command. L and N recorder included in the instrument. Manual switch sets range.

SIGNAL APPLICATIONS, FEEDBACK CONTROL

Safety Interlocks to overcome problems due to interruption of gas supply.

Figure 5. Diagrammatic representation of Ionics model 1224 TOC and TOD

ENVIRO-CONTROL–TOD

Patent restrains use of device for TOC

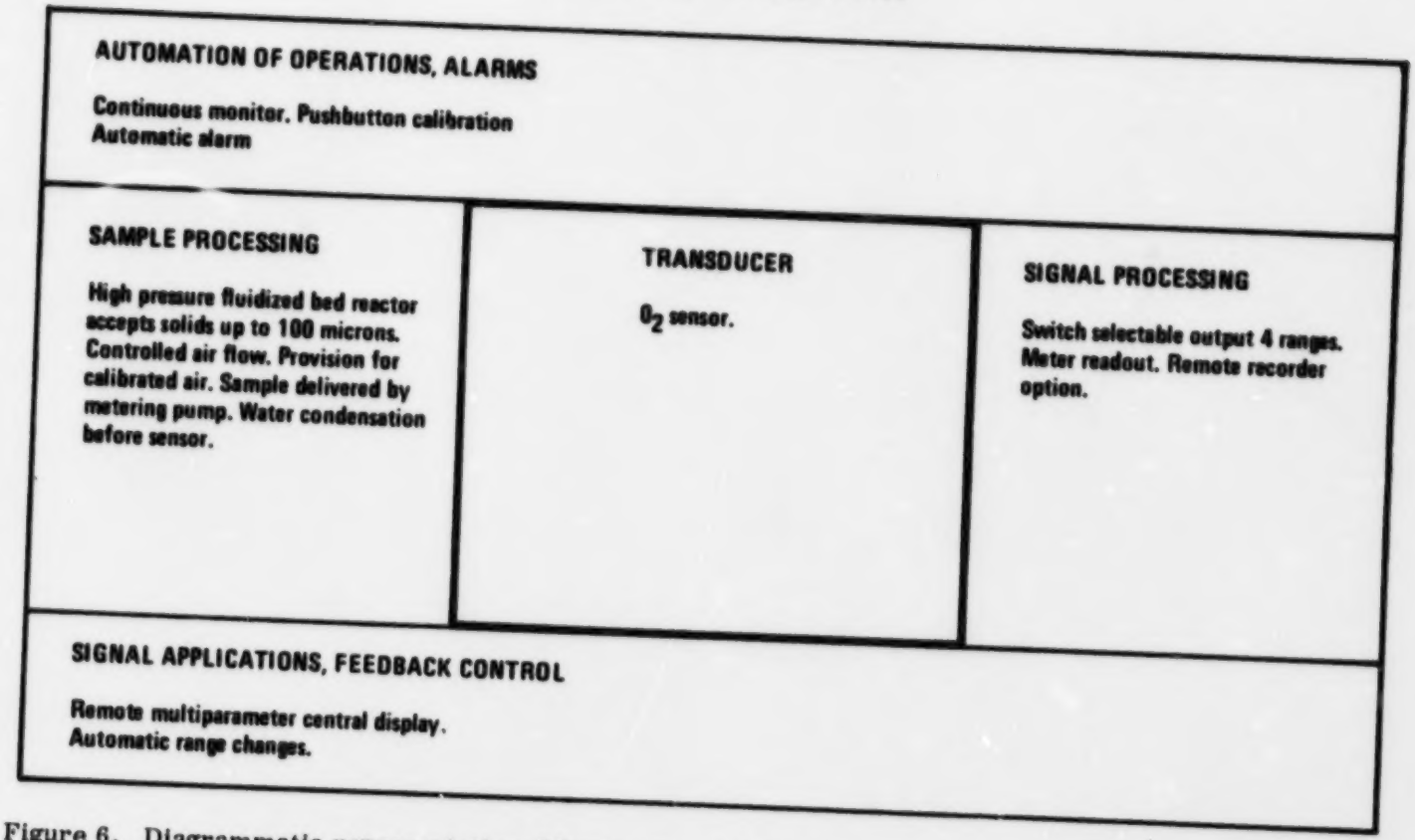

AUTOMATION OF OPERATIONS, ALARMS
Continuous monitor. Pushbutton calibration
Automatic alarm
SAMPLE PROCESSING
High pressure fluidized bed reactor accepts solids up to 100 microns. Controlled air flow. Provision for calibrated air. Sample delivered by metering pump. Water condensation before sensor.
TRANSDUCER
O_2 sensor.
SIGNAL PROCESSING
Switch selectable output 4 ranges. Meter readout. Remote recorder option.
SIGNAL APPLICATIONS, FEEDBACK CONTROL
Remote multiparameter central display.
Automatic range changes.

Figure 6. Diagrammatic representation of Enviro-Control TOC (patent restrains use of device for TOC)

ASTRO ECOLOGY CORP Model 1500 TOC and TOD

AUTOMATION OF OPERATIONS, ALARMS Pushbutton selection of TOC, TOD and TC Multiple sampling, options available Alarms		
SAMPLE PROCESSING Continuous sampling or discrete injected samples delivered to catalytic combustion tubes. Air pump. Handles suspended solids. Condenses water to form liquid waste. Gas stream delivered to the Lira.	**TRANSDUCER** NDIR Lira Non-dispersive Infrared Lira	**SIGNAL PROCESSING** Lira delivers signal to a meter.
SIGNAL APPLICATIONS, FEEDBACK CONTROL Meter		

Figure 7. Astro-Ecology Corporation model 1500 TOC and TOD

Although the Ionics TOC or TC analyzer cannot readily accept samples with suspended solids, intensive conditioning through use of a batch homogenizer permitted Dr. M. Zeitoun of Dow Co. to analyze mixed liquor sample for total carbon. He found that homogenization is the most critical process with dilution ratios and residence time dramatically affecting the results. In Dr. Zeitoun's opinion, the complex nature and moderate reliability of the batch, draw and fill sample conditioning system limits the usefulness of this system. Moreover, the maintenance experiences of Dupont's staff with the Ionics TOC analyzer clearly indicated the complex nature of flame ionization detection.

User comments with regard to the Astro-Ecology TOC analyzer point up the potential noisy data or long response time problems. Several users commented on noisy data during the combustion of solutions which contain organic compounds that are solids at room temperature and during the combustion of samples containing large particle suspended matter. Almost all of the Astro TOC analyzers exhibited corrosion problems that could be corrected by replacing all metallic components with Inconel and by properly insulating (adiabatic transport) the gas delivery tubing. In spite of the hopeful nature of the Astro TOC analyzer, no user data on accuracy, noise, drift, and response time, and on the ability to analyze samples with high suspended solids are available.

Liquid phase oxidation via acidulated dichromate to determine TOC as practiced in the Calibrated Instruments device is prone to interferences from chlorides, partial oxidations and loss of volatile organics. Accordingly, the accuracy of this device is poor. Because of the slowness of liquid phase oxidation, twenty-minute-response times are expected.

In closing, the field experiences of several users show that the complicated flame ionization detection approach of the Ionics instrument is less reliable

and requires more maintenance than the simple, straightforward infrared detection used by Astro-Ecology. Furthermore, continuous analyzers experienced fewer problems with sample delivery and injection than batch, sampling-valve-type instruments. Because of the high suspended solids concentration of storm and combined sewage, it is essential to homogenize the particulate matter to such a degree that representative samples can be transported through the analytical system; demonstration projects of Dow Co. have shown this to be a difficult but solvable problem. To prevent corrosion-type failures, careful consideration should be given to material selection and insulation, since the hot halogen gases and condensate have demonstrated their highly corrosive nature in several field applications. The possibility of changing the stripping acid from HCl to H_2SO_4 should also be examined as a method of eliminating or minimizing corrosion problems. Problems identified in the field applications will be addressed in the development of a storm and combined sewage monitoring system.

SECTION VII

PERFORMANCE SPECIFICATIONS

Most of the design goals as delineated in subject "Scope of Work" address the mechanical and environmental aspects of an organic monitor suitable for analyzing storm and related wastewaters. In this section, Raytheon's project staff expands on the performance design goals in light of the previous discussion on stormwater characteristics. The important organic-monitoring-system specifications are presented in chronological order of a storm and subsequent TOC analyses.

START-UP

Because storms are random events with a conditional probability of occurrence based on weather forecasts, seasons and geographical location, it is essential for a stormwater-organic-monitoring system to be on-line, producing valid data within five minutes or less of the command signal. The start-up command can be generated by liquid level sensors or rain gages.

SAMPLE PROBE

Available storm and combined-sewage data indicate that the vast majority of the organics present are soluble and small particulate matter (i.e., less than 10 mm). Accordingly, the sample probe should accept organic particles

less than or equal to 10 mm, reject larger material, and exclude grit and other dense particles. Moreover, the sample probe should take samples from the midstream section of the stormwater or combined sewer.

SAMPLE CONDITIONING

It is essential that the suspended matter contained in the sample be reduced to particles less than 0.2 mm (specific gravity ≤ 1.1) in any direction prior to induction into the analytical section of the TOC monitoring system because the particulate material should be within the region of Stokes Law; otherwise it is difficult to transport and analyze a representative sample. In essence, the conditioning equipment must be capable of reducing 10-mm particulate matter to less than 0.2 mm (maximum dimension) suspensions. All stringy, fibrous material should be suitably "chopped" to conform to the 0.2 mm specification.

SAMPLE TRANSPORT

To effectively transport storm and combined sewage samples, a minimum velocity of 61cm/sec (2 ft/sec) is needed. Additionally all connections, coupling, etc., should use sanitary-type fittings. A sampling line should never be dead ended.

SAMPLING RATE

Because the organic concentration of storm and combined sewage changes very rapidly, it is essential to have sampling rates greater than one sample per minute; it is desirable to continuously analyze the organic content. (Raytheon's proposed TOC-monitoring system utilizes continuous monitoring practices.) Slow sampling rates lead to loss of meaningful high-frequency information.

RANGE

During the initial phase of storm events, the increased flow scours the collection system and the organic concentration increases considerably above normal levels—the "first flush" phenomenon. The analytical components of a stormwater and combined sewage monitor should be capable of analyzing samples with TOC concentrations from 0 to 1,000 mg/l. As the storm progresses the TOC concentration usually decreases to about 200 mg/l. Wide, but time-phased TOC variations associated with storm-related waters may make a two-range instrument desirable: 0—400 mg/l TOC and 0—1,000 mg/l TOC. When the TOC exceeds 70 percent of the first range, 280 mg/l, the instrument should automatically switch to the higher range; conversely, when TOC concentrations decrease below 20 percent of the high range, 200 mg/l, the device should switch into the lower range. However, consistent with the theory of keeping the instrument as simple as possible, the feasibility of a single range (0—1000 mg/l) instrument should first be investigated. In this single range instrument, it is expected that the sensitivity will be adequate to provide the necessary precision.

SUSPENDED SOLIDS

Because of the first flush phenomenon, the TOC-monitoring system must accept and produce valid data on samples with a suspended-solids concentration from 0 to 8,000 mg/l. This is consistent with the 0—1000 mg/l TOC table, since many of the suspended solids are inorganic in nature. The monitoring system should be free from plugging by variously sized suspended matter.

SENSITIVITY

During storm events, a 15 mg/l change in TOC represents a meaningful change in composition. Accordingly the TOC-measuring system should have a 15 mg/l

limit of detectability and sensitivity in the low range. For the high range, 1000 mg/l, a 50 mg/l sensitivity is sufficient. For a single-range instrument, a 20 mg/l sensitivity should suffice.

ACCURACY

Whenever a measuring device is used for historical-data acquisition or in feed-forward control, the highest degree of accuracy possible is usually expected. Since many stormwater-organic-monitoring applications involve measuring of the organic load, and sometimes address feed-forward applications, obtaining high accuracy is justified. The best available technology should yield 5% of full-scale accuracy for the organic-monitoring system.

REPEATABILITY

The ability to obtain repeated readings under the same conditions is essential for feedback, and other control systems. Because many stormwater-TOC-monitoring applications encompass control of treatment processes, a precision of 3% of full scale is required. Additionally, the system output should be linear (±5%) over the range.

RESPONSE TIME

Since the aqueous organic concentration fluctuates rapidly during storm events, response time—especially in real-time control applications—should be as short as possible. Presently, a 5-minute response time appears to be desirable. The principal lag is the inorganic-stripping devices that are necessary for TOC determination; on the other hand, total carbon determinations should have shorter response time, since a stripping device is unnecessary.

ALARM FUNCTIONS

Stormwater and combined-sewage-monitoring stations are frequently located in remote areas. As such, a TOC instrument may not receive periodic inspections, and alarms are necessary to alert a central monitoring location to dispatch a repair crew. Alarm systems should monitor the temperature, sample flow, oxygen flow, and water flow. If an alarm condition exists, the instrument should automatically institute corrective action to prevent damage to these devices.

AUTOMATIC ACCESSORIES

The remote location and unattended operational goals of a stormwater and combined-sewage-organic-monitoring system clearly dictate automatic calibration of the TOC analyzer. Accordingly, the system must be capable of auto zero and span adjustments on a timed or external command basis.

SHUT DOWN

After the cessation of significant flows, the TOC system should shut down on flow rate or liquid level signals. The analyzer, moreover, should be readied for the next storm event. Shut-down procedures would include automatic calibration, flushing with purge water, and system calibration. The TOC system should be in stand-by mode, ready for the next storm event.

DATA INDICATING, TRANSMISSION AND RECORDING

To provide information for management and control, the TOC data, an analog signal, must be capable of being transmitted to a central location, usually located several miles from the monitoring station. Accordingly a standard instrument

output of either 0—5 volts dc, or 0—100 mVdc, or 4—20 milliamps is necessary so as to interface with standard telemetry systems (i.e., tone, frequency shift, or pulse duration transmitter/receiver systems). In most cases, a local recording device is unnecessary, because of the remote recorders. Local indicators, however, are desirable to facilitate TOC-analyzer and transmitter calibrations.

PERIODIC EXERCISING

As with other storm-related equipment, it is good practice to periodically exercise the TOC system during extended dry intervals. The developed TOC system, accordingly, should be capable of operating on a simulated sample upon command.

MAINTENANCE REQUIREMENTS

Most commercially available TOC analyzers require an analytical chemist or a very highly trained technician for proper operation and maintenance. Many municipalities simply do not have these highly qualified personnel. Consequently, the developed TOC system should be designed so an alert operator, plant mechanic or electrician can service the system with a minimum of training (about a week). Inevitably, simple maintenance requirements dictate a well thought out, but simple design which uses ruggedized components.

SECTION VIII

ESSENTIAL COMPONENTS FOR A STORMWATER ORGANIC MONITORING SYSTEM

The following unit operation and hardware describe the "best" choice assembly that is necessary for the automatic determination of TOC concentration of storm and combined sewage.

Table 5. OPERATIONS AND COMPONENTS NECESSARY FOR TOC DETERMINATION

Sample Unit Operation	Component
Sample Taking Sample Transfer	HydroSpace—Challenger System
Homogenization	Raytheon's Homogenizer
CO_2 Stripping Sample Delivery	Raytheon's Simultaneous Delivery and Sparge System
Unit Processes	
Combustion	950° Reactor (oxygen)
Reactor Regeneration	Flushing
Combustion Product Unit Operations	
Condensation & Cooling	Conventional Heat Exchanger
CO_2 Detection	Infrared Detection
Automatic Accessories	
Start-up/Shut down	BIF Cronoflow Level Detector
Zero & Span Adjust	State of the Art Engineering Design
Data Acquisition	Analog Recorder or Digital/Signal/ Processing

Figure 8 illustrates the series nature of these processes. Although a detailed discussion with regard to the reliability and availability of suitable components follows, it is profitable to review each function at this point.

In the case of a sample system, the sample preparation requires that the grinding and blending of the raw sewage should accommodate all the varied materials that are present in sewage. This must be done with continuous supply of sample and with homogenization of the components of the Total Organic Carbon that would normally contribute significantly to the information of interest. The processing of sample at this point can introduce non-representative signal, or noise to the system. The reactor system supplies heat and oxygen to support combustion of the sample. The geometry and material used in this design must consider effective heat transfer and corrosion. Because of the buildup on refractory materials, the reactor should be regenerated periodically. The condenser system can be expected to operate routinely. Fog occurs when inefficient cooling is provided, and condenser design should maximize heat removal.

The sample system is an assembly of components designed to grind and blend the raw sewage, transport it to the area of analysis and deliver a quantitative sample to the area of reaction in a composition that is characteristic of the material entering the system. A system of this type must be free of hangups and operate so as to maintain the sample in a liquid or suspension up to the point of delivery to the reactor.

The reactor is the component in which the quantitative sample is mixed with oxidizing gas and brought to temperature. At about 950° C, there occurs rapid evaporation of water and oxidation of carbon to CO_2. This process results in the accumulation of refractory solids that must periodically be purged from the reactor.

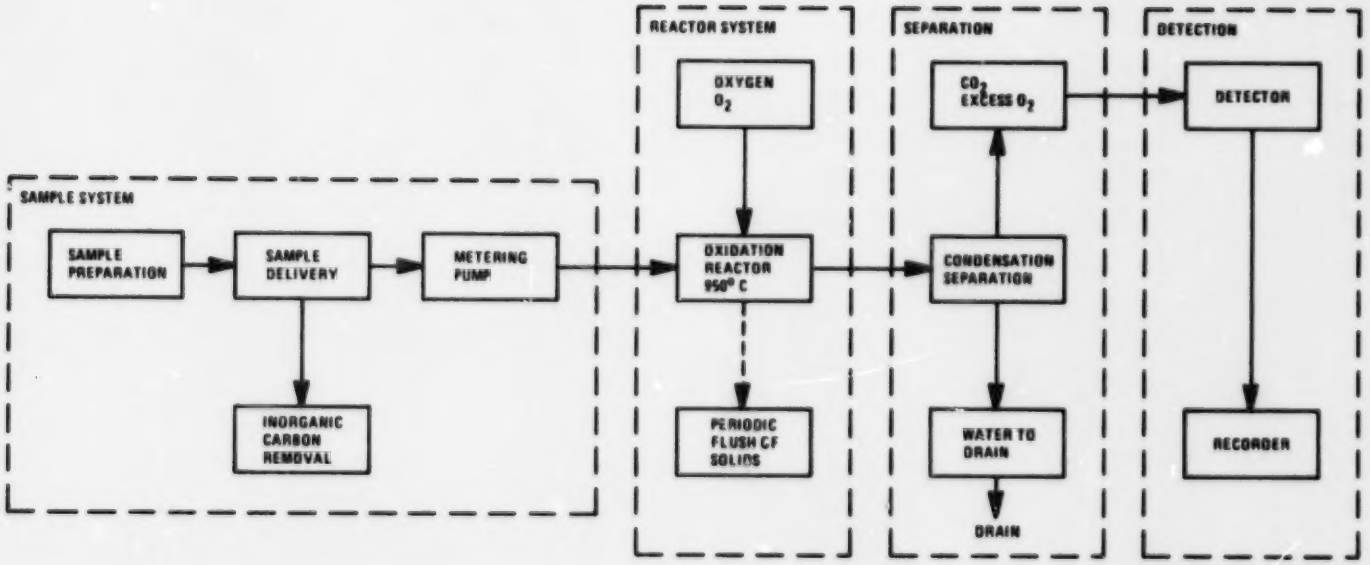


Figure 8. Block diagram of TOC

In the separation process a mixture of gases is treated so as to isolate for measurement the component of interest, carbon dioxide. In order to do this, the gases are passed through a water-cooled condenser where water is separated to a drain. Fog is coalesced and the carbon dioxide passed to the detector with the unreacted oxygen.

In the detector, a signal is developed. The signal is delivered to a meter and recorder to provide a permanent record of the Total Organic Carbon in the sample stream.

The choice of components to be used in the design of an on-line organic monitoring system involves a series of tradeoffs. These tradeoffs are dictated by concern for cost, reliability, maintainance requirements, economy of design and the need to interface with other components.

THE SAMPLING SYSTEM

Analytical systems are designed to operate on either continuous or discrete samples. Continuous samples are delivered to the sample process at a constant rate; whereas, discrete samples are generally delivered at a constant volume. While sampling of a constant mass might be of considerable value in the case of suspensions, the technology necessary to accomplish this has not been developed. Even though Raytheon plans to utilize continuous sampling principles, a brief description of a discrete system was included for completeness.

CONTINUOUS SAMPLE SYSTEM

In the case of stormwater TOC, where uninterrupted information is desirable, a continuous sampling process is necessary. Continuous sampling has the advantages of delivering an analog signal to the readout proportional to the TOC of the system, and has a better sensitivity due to a constant background.

For the continuous analysis of stormwater, it is necessary to provide means to transport a representative sample from the sampling point to the TOC system. The automatic sampling system required for this purpose must have the capability of operating continuously in a stormwater stream containing varying amounts of suspended solids. To prevent sample line plugging or blockage, a grinder is required to break down the debris or suspended solids to a pre-determined size such that unobstructed sample flow can occur.

Commercial units are available that are suited for this function. They contain a sufficiently powerful pump to maintain a high flow (typically 40-80 liters/min) which prevents solid settling in a correctly sized sample line (min. velocity 61cm/sec, 2ft/sec). The best grinder pump, based on our experience is the Hydro-O-Grind made by the Hydromatic Pump Co., because it has the ability to grind suspended solids to approximately 6.5mm (1/4") with an adjustable flow rate.

The ground sample is then passed to a homogenizer (Figure 9) for further processing, to fine particles (less than 100 microns).

Although several batch homogenizers are marketed, virtually no small size continuous duty homogenizers are commercially available. Raytheon's Environmental Systems Center, recognizing the need, developed and tested a suitable homogenizer. This device contains cutters as well as grinding surfaces. To date, Raytheon's team has experienced good particle-size reductions in a local waste-treatment facility while operating on raw sewage (Table 6). The in-line blender, Figure 9, has operated several months without failure. Raytheon's experience with this unit has been quite favorable. We have operated it continuously for several weeks.

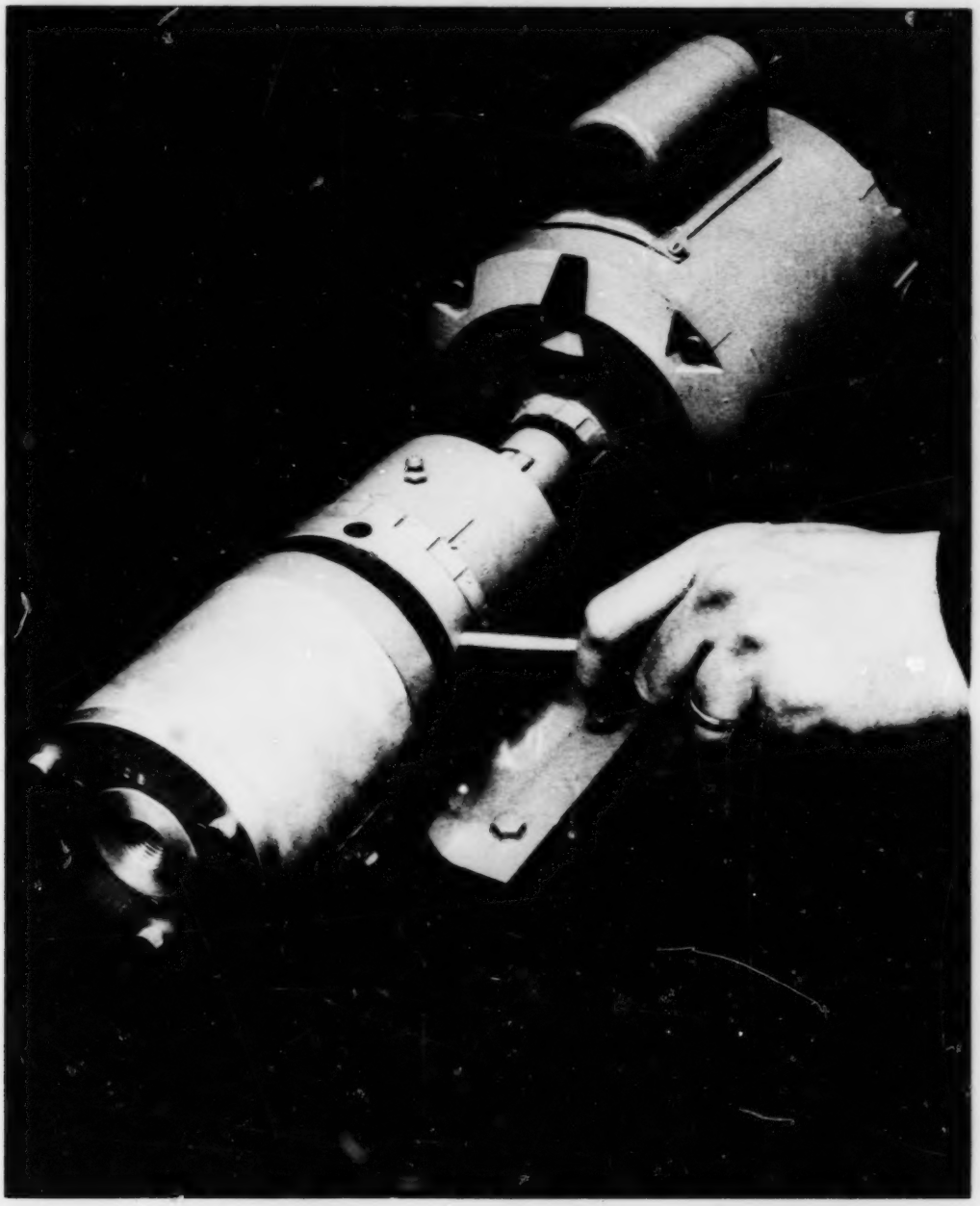


Figure 9. Raytheon's blender

Table 6. PARTICLE SIZE REDUCTION

Source	Batch % <110μ	Homogenizer Effluent % <110μ	Net Reduction
Secondary Clarifier Effluent	100	100	—
Raw Sewage	58.2	81.1	41.1%
Primary Effluent	66.8	85.5	22.0%
Mixed Liquor	82.6	87.9	6.9%
Secondary Sludge	65.6	77.9	18.7%

DISCRETE SAMPLE SYSTEMS

Discrete volume sampling delivers data in terms of grams/unit volume. An assumption about the density, is required to develop data in terms of percentages. The usual method of delivering a fixed volume to a sample stream employs a slider valve. Slider valves are designed to transfer a fixed volume through a surface seal. Suspensions of the type encountered in sewage could be expected to abraid the surface, damaging the seal after a short period of operation, and plug the valve. With this in mind, instrumentation based on slider-valve sampling of non-descript suspensions could not be practically applied to sewage. A more suitable method for handling a discrete sample of sewage is with the following trapped volume technique which provides two samples per cycle. This is by far the simplest and cheapest approach to sampling a suspension and might be used when discrete samples are necessary (Figure 10).

INORGANIC CARBON REMOVAL

Wastewater streams contain both organic carbon and inorganic carbon. Since the inorganic carbon is present as carbonate, there are two methods of separating organic from inorganic carbon. The first measures the inorganic carbon

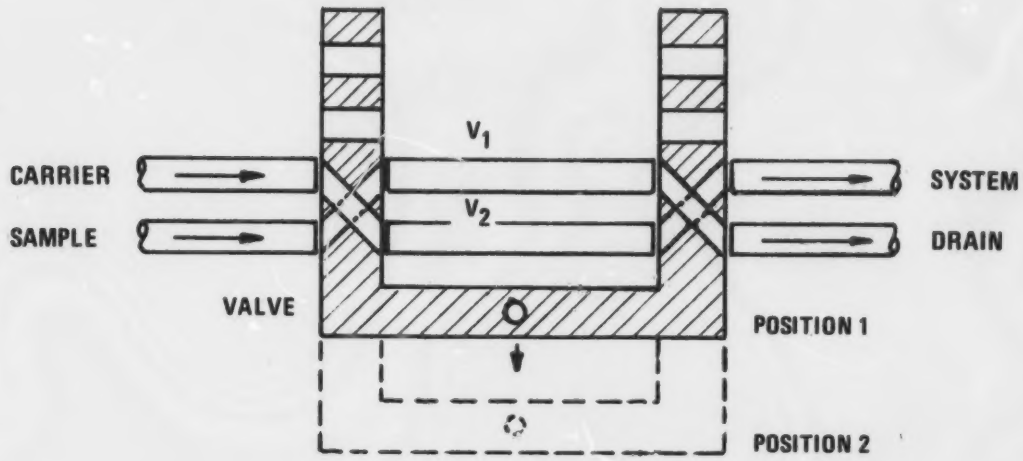


Figure 10. Discrete Sampling Valve Diagram

concentration separately, and the second removes the inorganic carbon from the sample stream prior to entering the high-temperature-oxidation furnace.

To obtain measurements of inorganic carbon and organic carbon, designers have provided for independent measurements of each. A furnace maintained at 150° C with an acid reactor is used to evolve carbon dioxide from the inorganic carbonate. A 950 ° C furnace converts both organic and inorganic carbon to carbon dioxide. Subtraction of the independent measurement gives TOC. The use of a low-temperature reactor to directly measure the inorganic carbon concentration in stormwater is not recommended because of the higher probability of solid plugging in the low temperature reactor. Suspended organic matter will not combust and accumulates in the reactor bed. This will require frequent maintenance which is generally to be avoided in automated instrumentation.

In the continuous removal of the inorganic carbon from the sample before oxidation of the organic carbon, the technique commonly employed involves acidification of the sample stream to a pH of approximately 1.5. The inorganic carbonates are converted to CO_2 gas which is stripped from the liquid phase by vigorous flow of CO_2 free gas.

Of the two methods, the CO_2 stripping technique is preferred because of its simplicity. One procedure successfully employed by Raytheon requires only a pump to add the acid and a source of CO_2 free sparging gas. Because of the extremely small demand, no commercial source of suitable sparging appartus is available. Raytheon plans to use a specifically designed proprietary device which has demonstrated its ability to accept sewage with a high suspended solids content.

SAMPLE AND REAGENT METERING (PUMPS)

The sample delivery system contains those elements that accurately mix the prescribed quantity of oxygen with the sample for conveyance into the combustion chamber. The need for continuous operation at a remote location in the presence of suspended solids in the sample places restrictions on the selection of these components. One of the components of primary interest is the pumping method of transferring liquids quantitatively and continuously. To do this reliably, the choice of a suitable pump design is of primary concern.

Pumps used in the transfer and precision blending of liquids are of essentially two types, either centrifugal or positive displacement pumps. These two divisions can be further subdivided with advantages and disadvantages listed in Table 7.

Table 7. PUMPING SYSTEMS

CENTRIFUGAL PUMPING	
Advantages	**Disadvantages**
Centrifugal	
The centrifugal pump is used for high gallonage at low pressures. It is not self-priming under normal circumstances. It will pump abrasive-laden chemicals as well as water. Different materials are used in its construction, as well as different types of shaft seals for a wide range of chemical handling ability.	The delivery system is susceptible to vapor lock as well as input and output stream pressure.
Turbine	
The turbine pump is similar to the centrifugal except that it is able to produce high pressures (150 psi) and low gallonage. Available in bronze and cast-iron construction. Use for chemical and water spraying, pressure booster service and boiler feed. It is not self-priming under normal circumstances.	The turbine blades could be expected to wear in a grit-bearing flow system.

POSITIVE DISPLACEMENT PUMPING	
Advantages	**Disadvantages**
Diaphragm	
The diaphragm pump uses the same principle as the old hand bellows. On the downward stroke the suction valve is opened to allow liquids and solids to enter. On the forward stroke the discharge valve opens (suction closes) and the liquid is forced out.	The precision of the delivery system is limited when used with solutions that contain any solids at all. This is because the seating of ball valves are the main consideration in the delivery rate.
Piston	
The piston pump is generally used for pumping low to medium viscous liquids at high pressures (to 1000 psi). It is self-priming at short distances. This type of pump is universally used in pressure wash applications.	Wear as well as valve seating limits the usefulness of the device.
Gear	
The gear pump is an excellent choice for pressures to 150 psi. It is self-priming and will handle an extremely wide range of chemicals because of the various materials of construction and seal choices. It is used wherever a self-priming pump is needed to handle viscous liquids, pumping oil for machine coolant, transfering viscous materials from one place to another, or for handling materials that will attack rubber or plastic. It will not handle abrasives.	Because it will not handle abrasives such as sand and gravel, it cannot be used with sewage.
Flexible Impeller	
The flexible impeller pump has more uses than any other type of pump. It is self-priming, will handle viscous and abrasive liquids, will deliver up to 100 GPM at pressures to 60 psi and is available in many choices of materials. It may be used as a general transfer pump for water and chemicals, as well as sanitary applications.	This will possible work for high flow rates but it exposes the internals of the system to the sand and grit in a sewer.
Peristaltic	
The peristaltic (tubing) pump is used for low gallonage extreme sanitary applications. Nothing comes in contact with the liquid other than the tubing itself. There are no seals or gaskets to leak or contaminate the fluids. It is self-priming, and will handle light abrasives.	Replacement of the flexible tubing is the limiting factor.

After a careful consideration of the various alternatives, it is apparent that only peristaltic pumps are compatible with the precision delivery of streams containing large amounts of suspended solids. For this purpose, we have used peristaltic pumping. An examination of the many commercially available peristaltic pump manufacturers leads Raytheon to choose Masterflex pumps because of the high quality, long life and ease of maintenance.

In the case of peristaltic pumping, wear and embrittlement of the flexible plastic is likely to be the limiting factor. The tubing might be expected to last from 3 months to a year. Maintenance should be provided during intervals of this duration.

THE REACTOR SYSTEM

In order to determine Total Organic Carbon in sewage, it is necessary that the water be rapidly removed from the sample and that the carbon compounds present in the sewage be volatilized, mixed with oxygen and allowed to undergo complete combustion. This operation requires a great deal of energy delivered rapidly and continuously. This process occurs in the reactor. Most TOC instrument suppliers use packed-bed reactors with various design configurations. In response to the need of high-heat transfer rates, non-plugging and complete combustion, a unique packed-bed reactor was designed and tested (see Available Test Data section). During the field survey, reactor design deficiencies were frequently cited as the principal problem area.

Some reactors employ catalytic surfaces such as cobalt oxide or copper oxide which are designed to hasten the rate of oxidation. Catalytic systems can complicate the problem of oxidation by promoting or inhibiting processes depending

on changes in temperature and catalyst poisoning due to surface contamination. For these reasons, catalytic oxidation appears impractical, and a non-catalytic fixed-bed reactor was designed, built and tested.

In our proprietary reactor design, the sample enters the water-cooled sample tube and is rapidly exposed to the high-temperature environment of the reactor. Droplets of water are evaporated. Energy is also required to superheat these gases. Because of the heat requirements of these processes a thermal gradient develops. This has been studied by making a number of temperature measurements at different positions in the reactor. These data are reported in Figure 11.

It is important to provide for efficient mixing and heat transfer to obtain rapid and complete combustion of the sample entering the reactor. In order to do this, a number of compounds were studied and data collected in an effort to recover total carbon in the sample. These data are reported in Table 8.

In view of the thermal gradient that can be expected in the reactor, it is reasonable to assume that the residence time is somewhat longer than would be expected from the equilibrium condition of the products at 950°C.

It is necessary that we demonstrate that our reactor design is effective for the purpose of total oxidation of the carbon content of the sewage sample. In order to measure combustion efficiency, several pure compounds were placed in solution at known concentrations. The total carbon was determined and compared with the theoretical value in Table 8. The results expressed give the percentage of theoretical organic carbon for the concentration indicated.

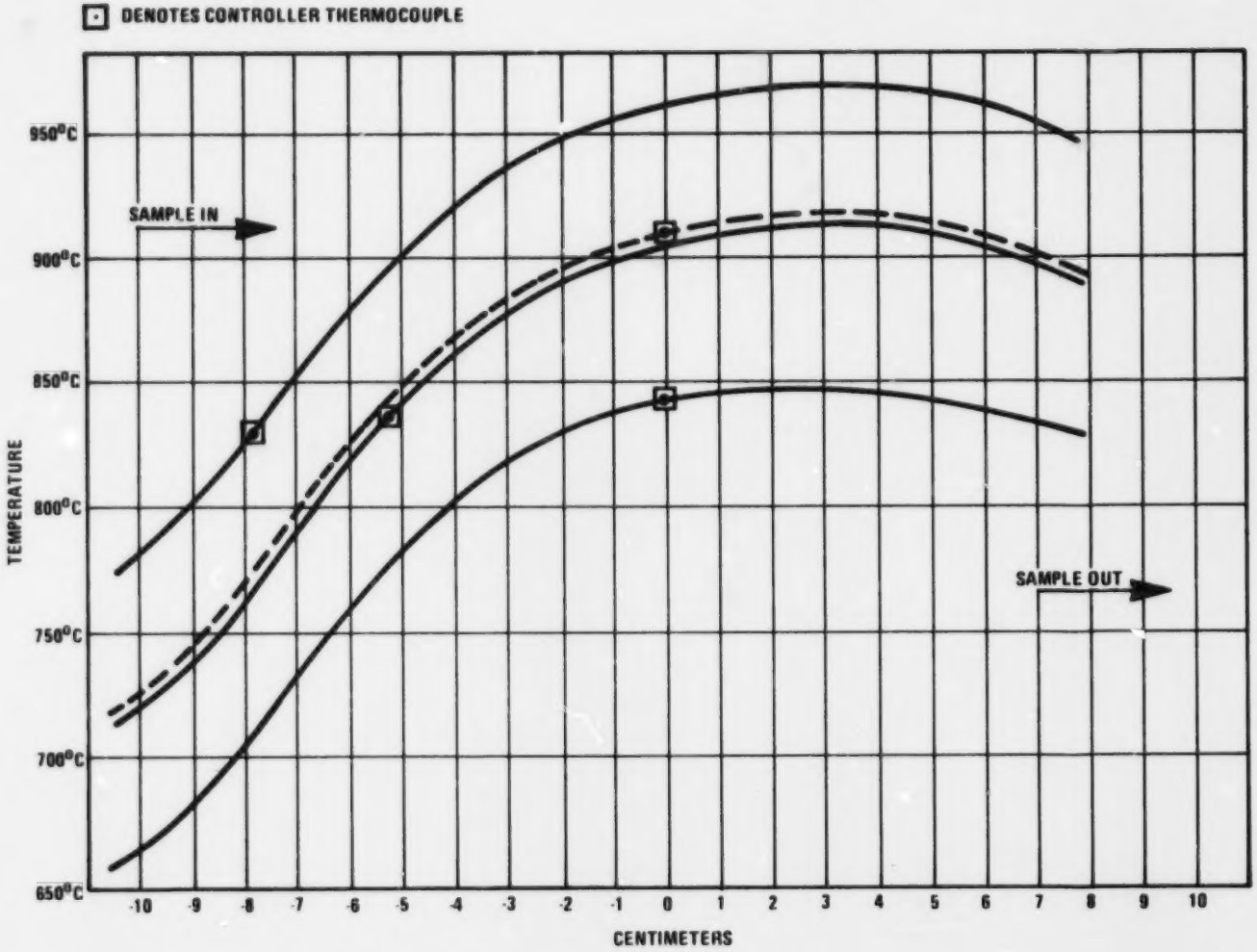


Figure 11. Temperature profile of the continuously operating reactor

Table 8. PERCENTAGE OF ORGANIC CARBON RECOVERED

From	.1% of Solution	5% Solution
Resocinol	98.6	99.0
Ethylene Glycol	99.4	98.3
Potassium Acid Pthalate	102.0	96.8
Cyclohexanol	100.7	97.3
2 Methal—3, 4, pentanediol	100.6	NR
Ethanol	99.7	NR
Oxalic Acid	103.3	96.5

It is only by virtue of the efficiency of mixing and heat transfer that Raytheon is able to achieve continuous combustion of samples under these conditions. Because a high combustion efficiency has been achieved at a flow rate of 3cc/minute, it is reasonable to expect that a safety margin exists for delivery at a lower rate. With delivery at a lower rate there would also be a lesser rate of buildup of refractory solids which would require proportionally less frequent flushing cycle.

OXIDIZING GAS

In its present design, the TOC uses oxygen as the oxidizing gas. The oxygen is introduced into the reactor as a pure gas. Future work is intended to explore the substitution of air for oxygen.

The oxygen obtained from either a compressed air cylinder (CO_2 free) or an air compressor requires a flow regulator to maintain a constant and precise gas flow. If an air compressor is used, the CO_2 present in the gas phase must be removed before the gas can be used as an oxygen source. A caustic liquid scrubber or solid phase absorption train can be used for this purpose. The

absorption technique might be best suited for the stormwater application because of the potential for automatic regeneration of the system. One possible absorption train consists of two separate columns of molecular sieves. The first (Linde 3A) would selectively absorb the water vapor, the second (Linde 4A) would absorb the carbon dioxide. Periodic heating of the absorption columns to about 150°C would be necessary.

COOLING AND CONDENSATION

Hot gases pass through a heat exchanger to reduce the water content in the gas phase, to prevent subsequent condensation in the sensor system. The cooling capacity of the heat exchanger has to be designed to maintain a constant humidity to prevent variation of the mole fraction of water in the cooled gas phase. A condensation trap is an integral part of the cooling system. The trap is designed to allow continuous condensate flow to waste while at the same time maintaining a sufficiently high head of condensate water to prevent the gas phase from escaping from reactor system to the atmosphere. Only a few inches of water are required for this purpose because the head is sufficiently small to act as a pressure relief value if excessively high pressures build up in the system. The actual volume of water required to maintain this head should be kept to a minimum to lessen the error because of the solubility of the CO_2 in the liquid condensate.

The products of combustion in the reactor are water and CO_2. This mixture of gases is passed into a water-jacketed condenser where the water is scrubbed from the gas stream and CO_2 is delivered to an infrared detector. The flow rate of the volatile products at the inlet is somewhat faster than at the outlet. Assuming adiabatic expansion out of the reactor and into the condenser, gas mass

velocity at the inlet is 18.56 liters/minute. At the outlet, it is about equal to the velocity of the oxidizing gas, 0.4 liters/minute. Consequently, large amounts of water must be removed from the stream at the condenser.

Residual water droplets and suspended particulate matter are frequently found in the flowing gas stream after it leaves the condenser assembly. Filters are required to remove these suspensions to prevent fouling of the CO_2 sensors. It is recommended that a vertical cylinder filled with a spherical solid of approximately 1/4" diameter precede the cartridge filter. It has been determined that the life of the filter is considerably lengthened because the major portion of the water droplets are mechanically removed in the vertical cylinder.

THE DETERMINATION OF CARBON DIOXIDE

Classical chemistry offers us a number of options for the determination of carbon dioxide. Carbon dioxide is an acid which has some solubility in water and base. It can be determined by measuring the change in conductivity of alkaline solutions. It can be used to precipitate barium and calcium salts. Carbon dioxide transmits visible light but absorbs infrared energy in the same way as most organic compounds. In contrast to similar compounds such as NO_2 and SO_2, it is an unreactive gas with a relatively simple chemistry.

INFRARED DETECTION

Organic compounds all have a distinctive infrared spectrum. The spectrum is more or less complicated as the compound is complicated. The simple compounds such as methane or carbon dioxide have a simple infrared spectra. Because of this, they are easily determined by infrared spectroscopy. There

are several approaches to the determination of various species by infrared spectra. These will be reviewed later. For our purposes, non-dispersive infrared detection was preferred. Non-dispersive infrared (NDIR) is an optimal technique for the measurement of a single component in a uniform and fairly simple gas stream. The principle of selectivity is in the design of the sensor. The gases flow through the light path resulting in energy changes as a result of absorption in a closed capacitance system.

The usual complaint about non-dispersive infrared (NDIR) is that it is not sufficiently versatile for the needs of a spectroscopic analyst. This, however, is not the problem in our analysis. For the purposes of an instrumental method for the determination of TOC, there is an interest in the analysis of one and only one component to the exclusion of interferences. NDIR gives us the method for obtaining the maximum signal from a minimum component concentration. The method of NDIR detection lends itself very well to the determination of CO_2 in our system.

The choice of the MSA Lira as an infrared detector represents a compromise among sensitivity, versatility and ruggedness of design. It provides an acceptable signal and sensitivity. This makes it possible to obtain a signal and to develop the data on concentration of TOC as low as 72 mg/l full scale with our present assembly. This is substantially better than necessary for sewage of almost any kind. Deionized water contains as much as 7 mg/l organic carbon as indicated by 10% full scale. The system has an easily modified range of operation and is easily adapted to the variety of operations and measurements that are a part of an experimental program.

The classical approach to infrared spectroscopy consists of the measurement of monochromatic signal from a black body radiator such as a globar. The monochromatic energy is developed through an alkali halide prism or by adjusting the spacing of an interference grating. This permitted a monochromatic infrared signal to reach the sample. The grating or prism is programmed so that a continuous spectrum of energy reaches the sample in time. The absorption in the sample is indicated by a measurement of photoconductance of one of several possible infrared sensors. Solid state narrow band gap materials such as PbS, PbSe and InSb are common sensors; thermistors, thermocouples and other heat detectors are also used. The absorption of energy by the sample results in a decrease in signal at the sensor and a consequent change in some electrical parameter of the sensor. There are several circuit designs in which a change of this kind can be monitored. The signal is usually delivered to a recorder. Continuous spectra are used for both qualitative and quantitative signal measurement. The optics of systems of infrared spectra are frequently crystals of alkali halide. They tend to require continuous maintenance and freedom from moisture. The instrumentation necessary to implement the classical measurement is expensive and does not lend itself to continuous monitoring equipment.

There are exotic approaches to the measurement of small quantities of hydrocarbon species in an atmosphere. Present designs available from Diax Corporation use monochromatic infrared lasers to energize gases flowing in a tuned cavity. There is a sonic source and a microphone in either end of the tuned cavity—all are tuned to the same sonic frequency. When the gas flowing through the tuned cavity absorbs energy of the monochromatic laser source, detuning of the cavity and decay of the microphone response result. The results can be used with several species and several lasers. Any species in the gas

stream can be effective in detuning the cavity. This system with readout can be obtained for $40,000. As such it appears to be prohibitively expensive for sewer monitoring requirements.

By contrast, there are relatively simple systems available from organizations such as Infrared Industries and Wilks that can be obtained in useful form for less than $1000. Instead of elaborate systems of spectral dispersion and selection they use filters. They have a relationship to infrared spectroscopy that colorimetry has to visible spectrophotometry. One often sacrifices sensitivity in this type of system, but sewer monitoring may be one of those areas where sensitivity may not be the primary concern in the infrared detector. Our choice of the Lira NDIR might yield to cost considerations and size limitations in future design. For the time being, however, the MSA Lira serves the purpose. Experience indicates that it lends itself well to this analysis. It is relatively trouble free.

ALTERNATIVES TO INFRARED DETECTION

Wet Chemistry

For the determination of CO_2, infrared analysis would appear to be the optimal approach. Several alternatives are possible and have been used in various applications.

The Wosthoff instrument for the determination of TOC provides a solution of sodium hydroxide that is passed through a system of differential conductivity

cells. The CO_2 evolved is passed into the flowing alkali system. The change in conductivity resulting from the formation of ions of CO_3 is monitored and reported as proportional to the total organic carbon burned in the sample.

Delta Scientific collects CO_2 in barium hydroxide solution and determines the light dispersed by the precipitate.

These are essentially wet chemical methods well known to ancient arts, such as winemaking. They suffer from the need for standardized reagents isolated from CO_2 in the atmosphere. The solution must be delivered to known concentrations by skilled technicians. They must be standardized and given more attention than is usually desired for maintenance of automated instrumentation.

Vapor Phase Chemistry

There exists a system (available from Lion Research Corporation) for the determination of CO_2 by passing a stream of unknown gas in a constant background into an ionizing radioactive (americium) environment. The higher cross section of CO_2 causes a greater ionization in a counter of suitable design. This is compared with the ionization in an input stream of uncontaminated gas. This is a technique that is used at fairly high levels of CO_2 and is employed in Gemini space flights as a means of maintaining the level of CO_2 in the confined atmosphere.

In a private communication from Dr. John Litzkowitz, we learned that a patent application on a CO_2 detecting device has recently been delivered to the U.S. Patent office. Because the detail was proprietary and not disclosed, it must be inferred from similar technologies. A crystal is made to oscillate at its characteristic piezoelectric frequency which is in part determined by its total mass. The adsorption of CO_2 on a resin-coated crystal changes its mass and

consequently its frequency. By monitoring the frequency, it is possible to monitor the CO_2. The resin is periodically recharged by flushing with CO_2 free gas.

Previously, in the early 30s, Zisman of the Naval Research Laboratories implemented this technique to detect adsorption on oscillating charged metal electrodes. His work was referenced by Chambers and Eaton in an effort to design an odor detector in the late 50s. The quartz crystal was used by King in his effort to design an organic and water monitor. It has been commercially employed by Dupont in the Dupont water monitor.

The problem with all these devices is that they depend upon a change in mass. Any mass will bring about a change in frequency. They are as good as they are selective. Oil and hydrocarbons will absorb and change oscillating frequency, also they require frequent calibration and recalibration. Since they are essentially integrating devices, the absorbing surfaces become saturated resulting in non-linearities and the need for frequent purging.

These problems may be overcome by careful design. In view of the long successful experience with other systems, the measuring principle will have to be confirmed by the test of experience before it can be recommended.

Recent publications[19] suggest the possibility of a reducible gas sensing electrode system. There is not a great deal of experience to establish these as useful techniques. As it appears, lanthanum fluoride was deposited by means of vacuum deposition on metal substrates of various materials. Signals were developed across this material in the presence of several oxidizing gases. The current measured from anode to cathode was found to be proportional to the

oxidizing gas. CO_2, NO_2 and SO_2 were among the gases with a reasonable signal.

There is hardware available from Johnson Laboratories for the determination of carbon fourteen in CO_2. If the carbon dioxide is enriched with carbon fourteen or concentrated in some way, it is possible to determine carbon by the combustion of any organic material. In the case of sewage, a measurement of this sort would be of considerable interest because it could be used to determine energy source products as a source of pollution. Petroleum and coal are radioactively dead carbon sources but living matter has a representative carbon fourteen concentration. The difference between total carbon and radioactive carbon would be the energy source carbon.

There are other possibilities that are even more speculative than the above but it is evident from the review above that infrared is the only practical choice and among the various techniques, non-dispersive infrared appears to offer the most practical compromise at the moment.

For the purpose of providing a comprehensive overview of the information in the previous paragraphs, we have prepared Table 9. This also includes some additional methods employed in carbon determination. Here we have addressed the various options and evaluated these options as they apply to sewage.

SAFETY AND ALARM SYSTEMS

It is possible to anticipate several problems in the abnormal operation of the TOC instrument. The occurrence of these events should give cause for alarm and attention. It is a characteristic of a well designed automated instrument that the alarming event should be signalled and corrected by automated instrumentation.

Table 9. THE DETERMINATION OF CARBON IN SEWAGE

Phase	Compound	Method of Determination	Comment
Liquid	Carbon compounds in solution	1) UV Absorption of Organic Compounds	Not specific for Organics Solids dispense the energy.
	Carbon dioxide	2) Collection of CO_2 in Barium Hydroxide measured by nephelometry	Requires supply and maintenance of reagent isolated from CO_2 in air. Subject to numerous interferences.
		3) Differential Conductivity	Requires supply and maintenance of reagent isolated from CO_2 in air. Subject to numerous interferences.
Gas	Methane CH_4	1) Flame ionization detection	Applicable for high sensitivity at low levels of carbon. Requires Catalytic reduction of Carbon Dioxide.
		2) Temperature of combustible gas mixture	Requires combustible gas which has to be formed first.
	Carbon Dioxide	1) Infrared Detector	
		a) Prism, grating filter devices	Passive detector system of high versatility of considerable sensitivity.
		b) Nondispersive Infrared (NDIR)	Passive detector system of high sensitivity and selectivity of a specific bond structure.
		c) Diax Resonance Cavity	Extreme sensitivity to mixtures of extremely small concentrations (1 part per billion) but expensive.
		2) Ionization of Gas by Americium and measurement of conductivity in the ionization chamber	Very reliable and passive system. Requires supply of radioactive source. Depends on the cross section of the species to radiative ionization.
		3) Absorption of CO_2 on resin-coated crystal oscillator	New technique likely to be non-selective in application.
		4) Conductivity of LaF_3 thin films in atmosphere of CO_2	New technique, but insufficient information to estimate applicability.

There are several sources of difficulty in which the operator might wish to shut down the instrument. One of these is a thermal runaway where the temperature controller is open circuited or disconnected resulting in a signal that calls for continuous heating of the reactor. This wou'd cause destruction of the instrument. We have provided for this eventuality by breaking the main line power

when the reactor reaches 1000°C, which is beyond the range of the control thermocouple.

A second source of difficulty might result from corrosion of components in the reactor. High temperatures and undefined acid conditions of the reactors can result in corrosion of the water-jacketed sample tube. The effect would be to deliver water from the cooling tube to the hot reactor resulting in a rapid cooling of the reactor and steam generation. This would cause high pressure and vapor evolution. Here a low temperature shutoff, would be of value, closing down power and flow to the water line. This should be associated with an alarm indication.

If sample flow is discontinued for any reason it would be useful to have this information available. In this case, the graphical readout would tend to zero on a continuous basis. It would be sufficient without shutdown to have a visual indication of the effect. A signal could be taken from the readout itself simply by placing a low level signal switch on the recorder.

A more serious condition would exist if the sample was delivered to a plugged reactor. This would result in an explosive buildup of pressure. A pressure gage would be a good indication of this condition. The present design incorporates a tygon tube connection that would serve as a blowout under a condition of excess pressure. There is also a pressure switch.

If oxygen were to stop flowing, a rotometer flow indicator could be used to indicate this and the signal developed to give a readout and to shut down the power to the instrument.

Water flow to the heat exchangers is about as important as oxygen flow and might be indicated in the same manner.

In spite of the importance of automatic controls and safety alarm, it is essential that we establish some routine preventive maintenance and inspection. The failure of a plastic tube or a pump might result in a serious nuisance such as a sewage spill. This prospect could be eliminated or greatly reduced by adherence to a routine inspection and replacement schedule, similar to the requirement of automobile and airplane maintenance.

The alarms, delineated in Table 10, are commercially available from several commercial suppliers at this time. Raytheon's staff has selected only the thermal runaway alarm system. As the laboratory test program matures, the remaining alarms will be appropriately selected.

In addition to alarms, automated features can be incorporated with digital control and signal delivery as described in Figure 12.

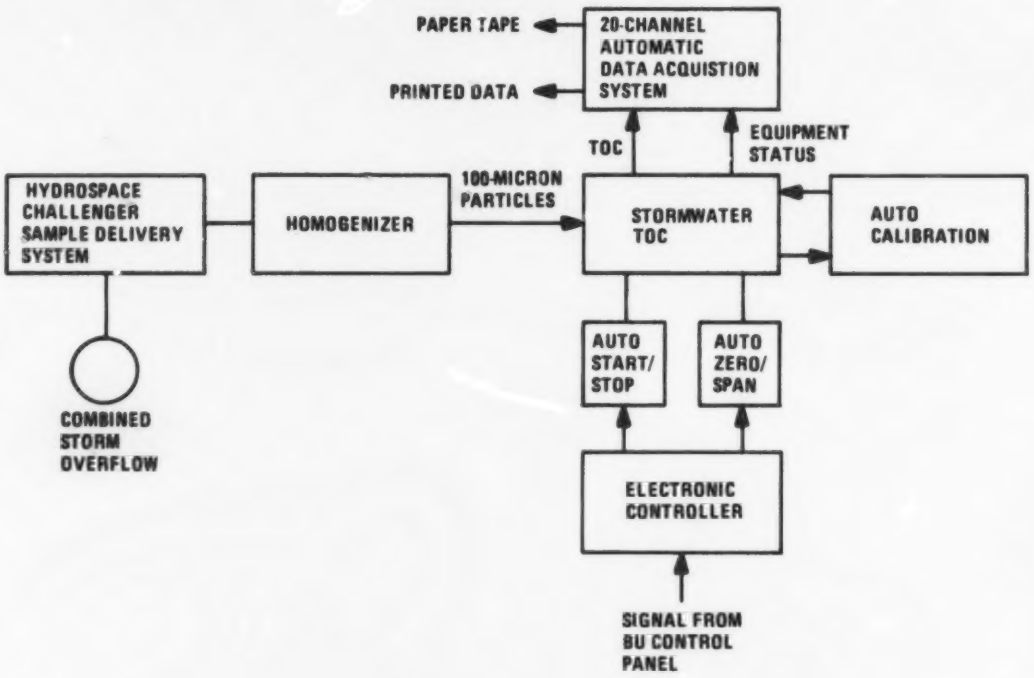


Figure 12. Field system diagram

Table 10. ALARMS

Alarm Condition	Sensor	Action	Hazards Due to Failure
Failure of temperature control of reactor	Thermocouple	Shutdown--repair or replace temperature control circuit	Thermal overrun will melt the Inconel.
Corrosion of sample cooled water jacket	Diaphragm pressure switch	Increased pressure causes automatic shutdown	Blowout of sample line
Sample flow interrupted	Recorder	Low level recorder switch causes sample pump shutdown	Uncontrolled sewage spill
Reactor plugged	Diaphragm pressure switch	Increased pressure causes automatic shutdown	Blow off of the sample tube
Oxygen flow stopped	Capacitor sensor on rotometer	Signal light and shutdown	Reactor will have incomplete combustion distilling carbon compounds which plug the reactor and condensor
Water flow stopped	Capacitor sensor on rotometer	Signal light and shutdown	Hot gases will flow to the NDIR contaminating the optical system

SECTION IX

A SYSTEM DESIGN FOR SAMPLING AND TOC MEASUREMENT OF THE STORM EVENT

In order to fully understand the requirements of a successful, rapid on-line stormwater organic monitoring system, it is advisable to review the proposed operating objectives:

- Large organic debris such as mattresses, rubber tires and two by fours cannot practically be included in the sample system and must be eliminated from sample intake orifices.
- A statistically representative sample containing suspended solids must be delivered from the sewer to the instrumentation without solid segregation because of settling or high velocity entrainment.
- The sample must be put in a condition for acceptance by the instrumentation that is ready to proceed with uninterrupted, continuous analysis.
- When the storm event is over, it is necessary to flush the equipment and shutdown the system so that it will be left in a condition to be turned on when necessary at a later storm event. In this section, we will consider these problems and reference the available technology to implement the design.

SAMPLE SYSTEM

Because of the significance of the suspended solids a carefully selected sampling system will be required for the delivery of a representative sample to the TOC system. This has been a problem of great concern to a number of people and there are a number of devices that have been used to sample sewers. Most of them are intrusion devices that would be demolished by the debris of a storm event. They have been evaluated in some detail by Shelley and Kirkpatrick[20] and are reported as inadequate for the purpose of making measurements on storm and combined sewage. With this problem in mind, Dr. Shelley of Hydrospace-Challenger has recently been contracted by the Storm and Combined Sewer Technology Branch of the EPA to design a sample transport and handling system that would be useful for the purpose of taking representative samples during storm events. The system which Dr. Shelley is assembling for this purpose is designed for storm sewer sampling and is intended to be adapted for use in the rapid, on-line organic monitoring field demonstration at Boston MDC-BU Station.

In a private communication with Dr. Shelley, it was learned that the system he is considering at present is as follows:

> A number of tubes are placed along the perimeter of the sewer oriented so as to present a downstream intake to the system with a minimal intrusion into the pipe. This arrangement eliminates gross solids and transfers the significant small size particles and organic liquids to the sampling system. Sample entering the system is transferred at velocity of 305 cm/sec(10 ft./sec.) by means of peristaltic pumping. Fluidic diverters are used to switch streams. The control and electronic system are completely solid state. Each sample intake has an

independent pumping system and stream diverter. The samples are delivered to a central compositing receiver which stores the sample. After several minutes of this operation, water is passed through the lines and a flush cycle is operated. This is completed and a new sample composite is synthesized.

The system as presently designed is intended for the preparation of discrete samples. It will be necessary to make several accommodations for the continuous sample delivery. The present system has a redundancy of sample delivery lines to provide a statistical sample. It should not be too difficult to program a portion of the system to deliver the sample while the other portion flushes. This should meet the needs of the continuous sample delivery requirement.

Since this sample delivery system has been designed for the purpose of preparing samples for analysis of data associated with the storm event and has been funded to meet the need for such a device, there is no reason to look for another.

TOC ANALYSES

After extensively reviewing the several alternative systems and selecting the components for the monitoring of storm and combined sewage organic content, it is appropriate to generalize the observations.

All carbon compounds oxidize. When this oxidation is complete there is only one product, carbon dioxide. The universality and simplicity of this chemistry is well suited to the principle of design of a Total Organic Carbon analyzer.

Because this product is stable, easily handled, non-combustible and generally well behaved, it is unnecessary to look to other compounds on which to develop an analysis of TOC.

Several TOC analyzers are designed around the catalytic conversion of carbon dioxide to methane and the further determination of methane by flame-ionization detection. The only justification of this approach would have to be based on the need for sensitivity to carbon concentration less than 10 mg/l. Sewage rarely contains so little carbon. The additional complication required for this approach are sufficient to exclude it from serious consideration as a means of determining Total Organic Carbon in storm sewage. The direct determination of the oxidized product of combustion, carbon dixoide is preferred for the purpose of continuous measurement of organic carbon in sewage. The greatest problem that had to be solved is sample handling and delivery. A considerable study has demonstrated that it is possible to prepare the sample to the necessary degree of uniformity to obtain totally acceptable data on a long-term basis with a dynamically flowing sample (see Figure 13). The present TOC has been designed with a NDIR detector that is capable of producing an uninterrupted signal to a recorder. For our laboratory model, a number of automated functions have been programmed into the internal control, operation and protection of the instrument. This arrangement is diagramatically presented in Figure 14.

In summary, the presented literature clearly shows that from all the available methods of measuring the organic content of wastewaters, vapor phase oxidation is the only method suitable for reliable, on-line, unattended operation. Among the options of monitoring the products of combustion, infrared detection of CO_2 is the most desirable technique because it is straightforward, reliable and

addressable by ruggedized equipment. However, the inability to accept samples with suspended solids and the accumulation of refractory material in the combustion reactors have impeded the development of a reliable, on-line TOC suitable for unattended monitoring of the organic content of wastewaters. Based on available technology and Raytheon's experience, (see Prototype Data section), development of a suitable stormwater and combined sewage organic monitoring system is feasible, if the suspended solids and refractory material problems are specifically addressed during design stages. The remainder of this report discusses Engineering Model Data and our schedule of testing and reporting on the developed system.

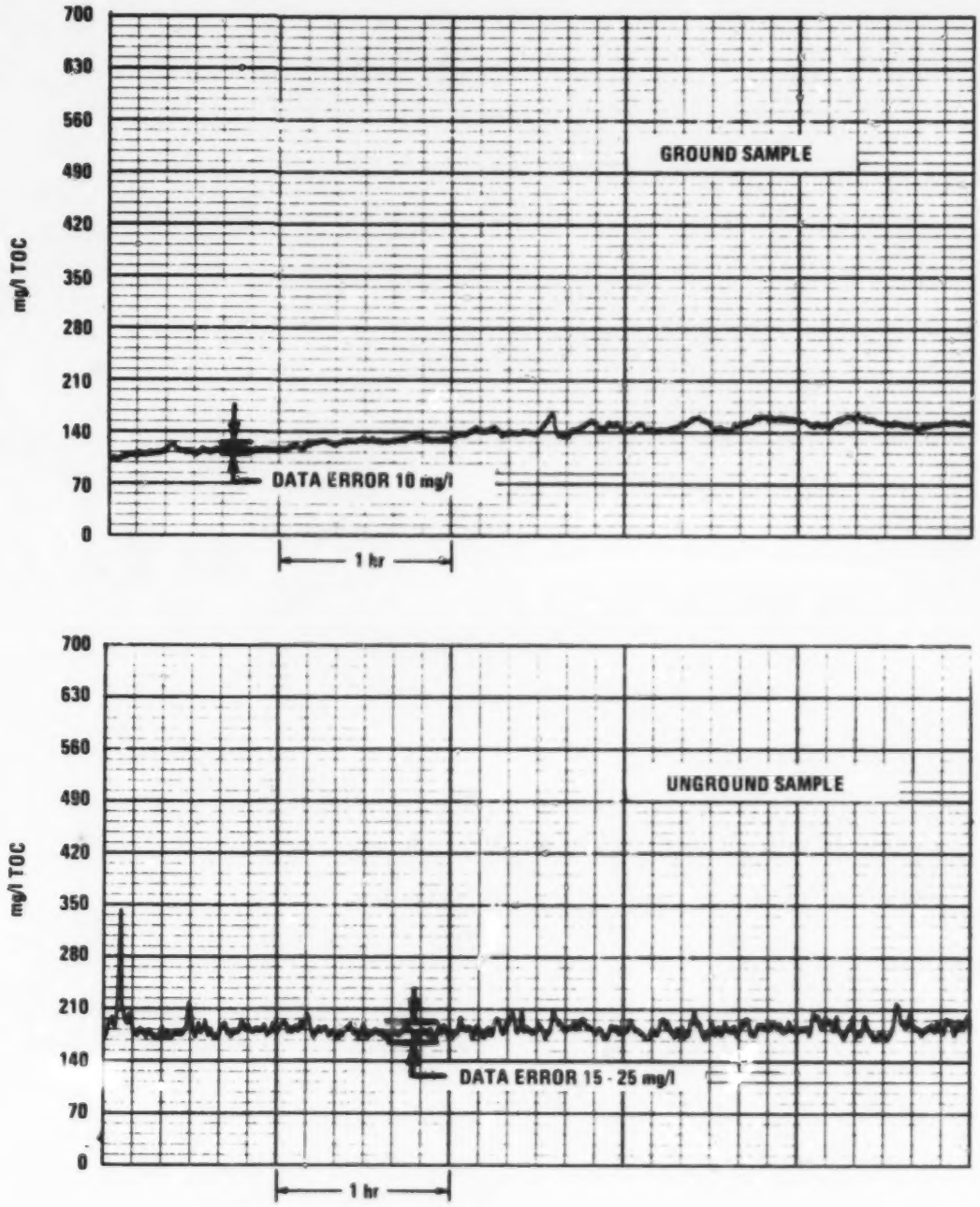


Figure 13. Continuous data on a flowing sample

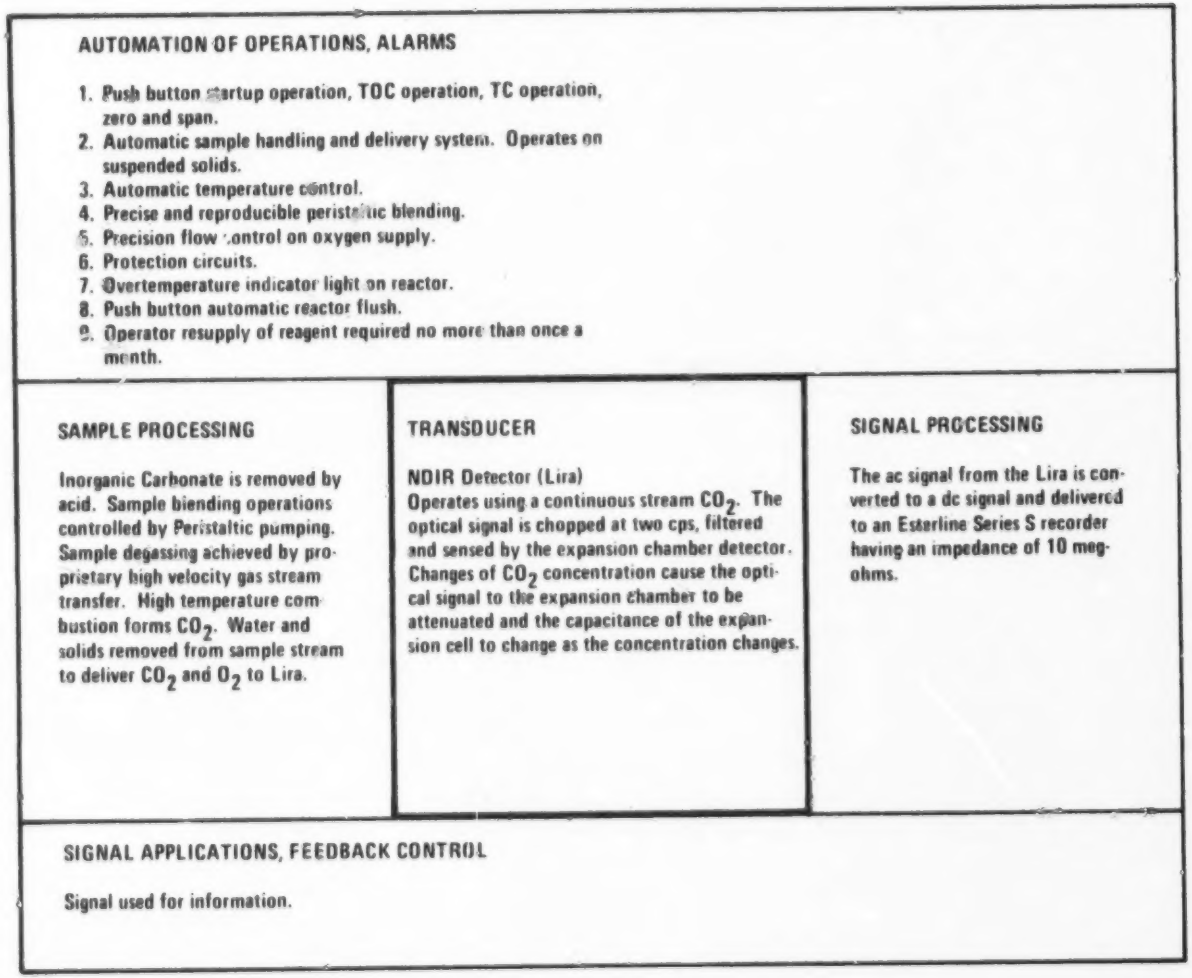

AUTOMATION OF OPERATIONS, ALARMS
1. Push button startup operation, TOC operation, TC operation, zero and span.
2. Automatic sample handling and delivery system. Operates on suspended solids.
3. Automatic temperature control.
4. Precise and reproducible peristaltic blending.
5. Precision flow control on oxygen supply.
6. Protection circuits.
7. Overtemperature indicator light on reactor.
8. Push button automatic reactor flush.
9. Operator resupply of reagent required no more than once a month.
SAMPLE PROCESSING
Inorganic Carbonate is removed by acid. Sample blending operations controlled by Peristaltic pumping. Sample degassing achieved by proprietary high velocity gas stream transfer. High temperature combustion forms CO_2. Water and solids removed from sample stream to deliver CO_2 and O_2 to Lira.
TRANSDUCER
NDIR Detector (Lira)
Operates using a continuous stream CO_2. The optical signal is chopped at two cps, filtered and sensed by the expansion chamber detector. Changes of CO_2 concentration cause the optical signal to the expansion chamber to be attenuated and the capacitance of the expansion cell to change as the concentration changes.
SIGNAL PROCESSING
The ac signal from the Lira is converted to a dc signal and delivered to an Esterline Series S recorder having an impedance of 10 megohms.
SIGNAL APPLICATIONS, FEEDBACK CONTROL
Signal used for information.

Figure 14. Proposed TOC

SECTION X

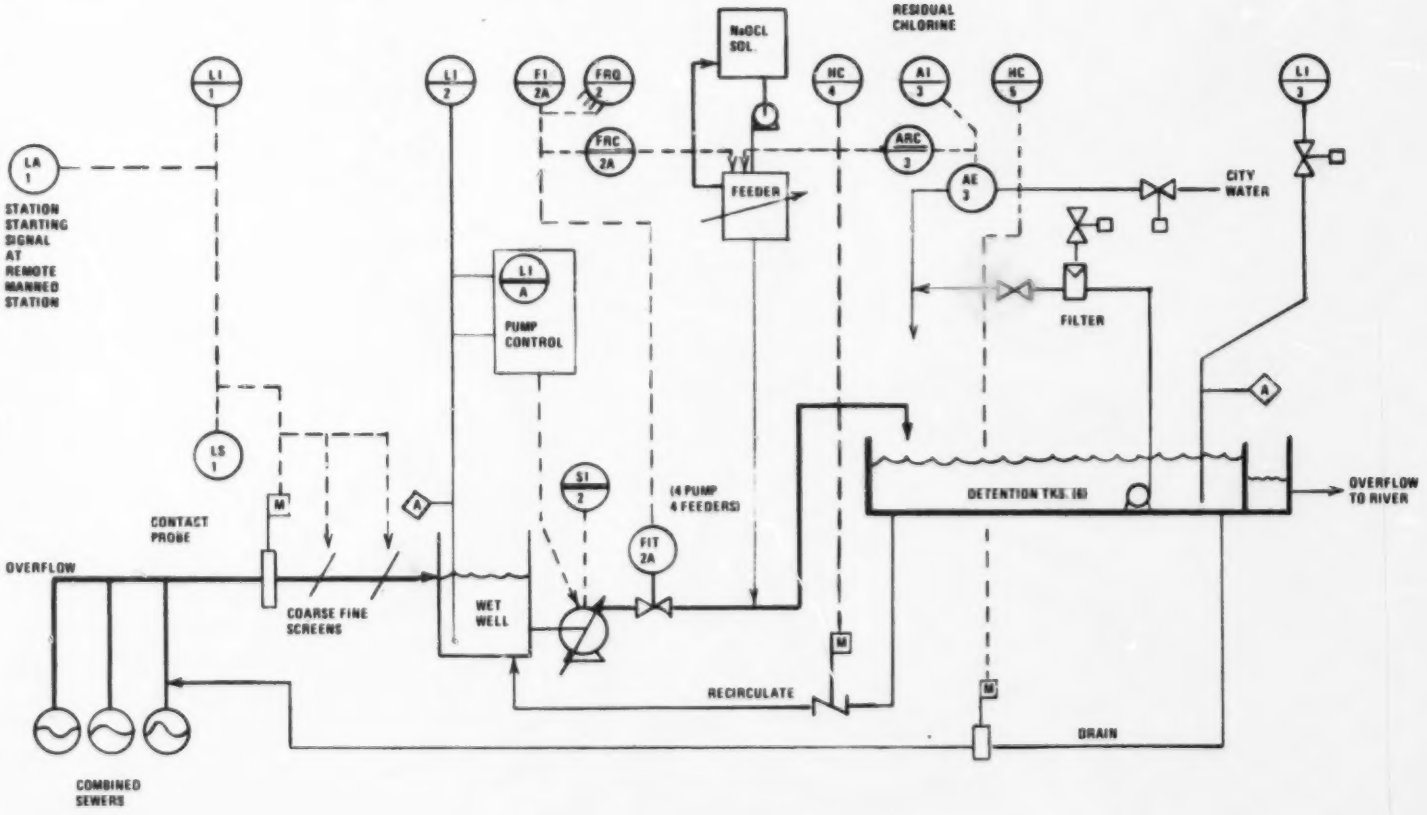
PROPOSED OPERATING MODE TEST SITE INTERFACES AND FUTURE ACTIVITIES

START-UP

The start-up of the analytical and sampling equipment can be sensed by a suitable level indicator as is presently done at Boston's MDC-BU installation. A bubbler tube device measures the wet-well level (loop 2, Figure 15). When this level reaches some predetermined value, a pressure signal is delivered to indicate this event and to start up the treatment processes. A device to deliver this signal is the BIF Cronoflow Transmitter Model 231-20 which provides signal telemetering where that is of interest. Raytheon plans to use the wet-well level signal to start stormwater sample flow to the organic monitoring system.

Specifically, the TOC analyzer will be standing by, already at operating temperature; the sample delivery and conditioning system will contain clean flush water (see stand-by discussion). When the wet well reaches a predetermined level, the sample delivery pump (Figure 16) will start transporting stormwater samples to the analytical train. The data acquisition system, automatic sample takers, and strip chart will also be started up at this time.

A signal received from the BIF transmitter might be used to operate a sequence timer that could be programmed to perform the necessary start-up sequence.



Note: Standard Instrumentation Symbols and Identification of the ISA

Figure 15. BU stormwater detention facility

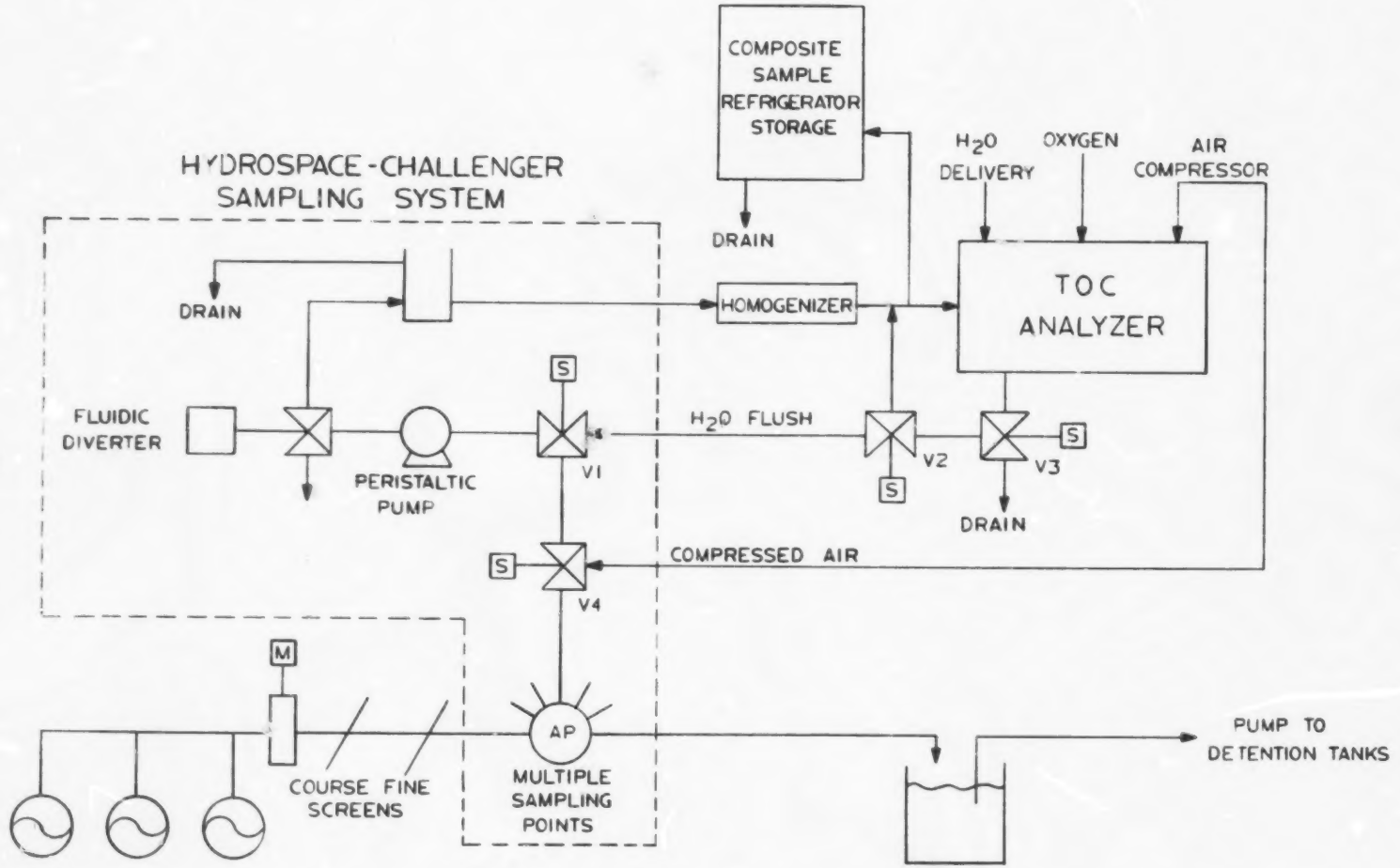


Figure 16. Application of sample system and TOC monitor to MDC-BU installation

A sensor of this sort would respond whenever the sewer level exceeded some predetermined level.

OPERATION OF TOC

When a suitable sample has been taken it must be delivered to an operating TOC instrument. The operation of the TOC instrument requires a continuous supply of air, cooling water and power. For the purpose of rapid response to the storm event, the furnaces must be at operating temperature, the sample tube and condenser must be cooled, and air or oxygen must be supplied for the exercise of the delivery system.

There is a need for peristaltic pumping throughout this instrumentation. If tygon pump vanes are allowed to remain compressed for an extended period of time, as would be the case of an inoperative peristaltic pump, they deform and eventually become brittle and crack. Since both the sample delivery system and the TOC instrumentation make extensive use of this type of pumping, our present design commits us to some type of continuous sample processing. If continuous sample processing is necessary, it is convenient to use water from the condenser-cooling operation as a sample. In a case of a sanitary system where relatively clean water is available at a short distance, only pumping would be necessary.

PERIODIC OPERATION

With our present experience in the long-term operation of the stormwater TOC and sampling systems, it is too early to predict whether it would be more desirable to operate continuously with sample delivery or remain idle with periodic exercise. It is evident that continuous furnace and infrared detector operation

will be necessary simply to eliminate the time to arrive at operating temperature when the instrument is needed for stormwater monitoring. This should not be a problem and can be implemented without serious inconvenience.

The exercise of the sample delivery system is possible by delivery of a signal from a 12-day clock timer. These are in common use on home water conditioners and have a good record of reliability. The clock timer can be used to activate a program timer that will autozero, autospan, and deliver water to the operative peristaltic pumps. A two-hour program timer such as those available from Singer's Industrial Timer Division should be adequate for this purpose.

While our ultimate design is expected to operate at a variety of locations, we intend to conduct our first tests in the Boston MDC-BU installation. This is, in fact, a well designed and well maintained stormwater facility where personnel might be expected to observe, report and provide data and operations so that maintenance can be supplied as needed.

Figures 17 and 18 are illustrations of the MDC-BU operation. Figure 16 gives a diagram of how this facility might be brought to interface with the Hydrospace-Challenger sample system. The diagram contains further description of how the sample system might interface with the stormwater TOC. Valves that interface the operation of the TOC with the sampling system are described in Figure 16. These valves are inserted to permit the diversion of air and water, to flush the sample delivery system and to deliver exercise sample to the TOC when it is intended to operate the instrument in the exercise mode. They can also be programmed to flush the sample system with both air and water as required by the Hydrospace-Challenger design.

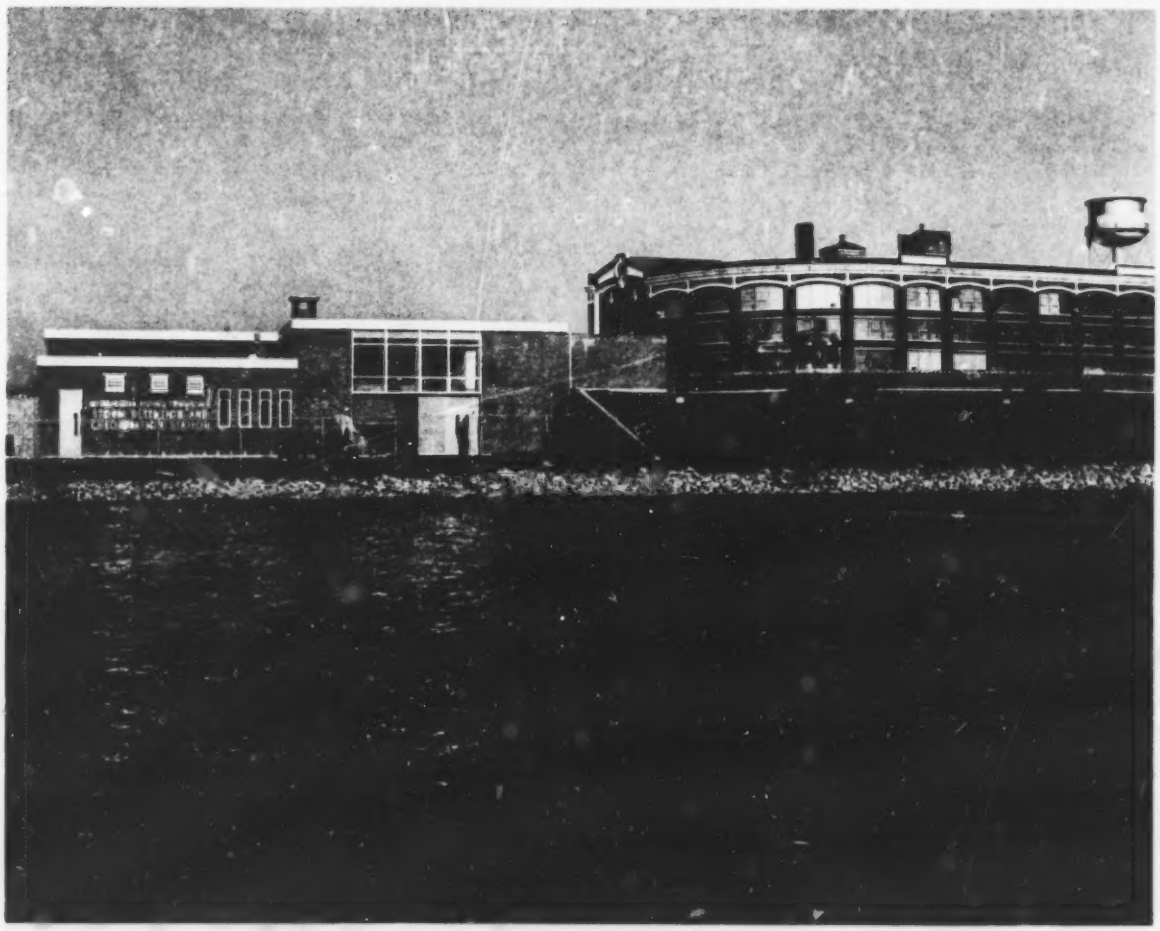
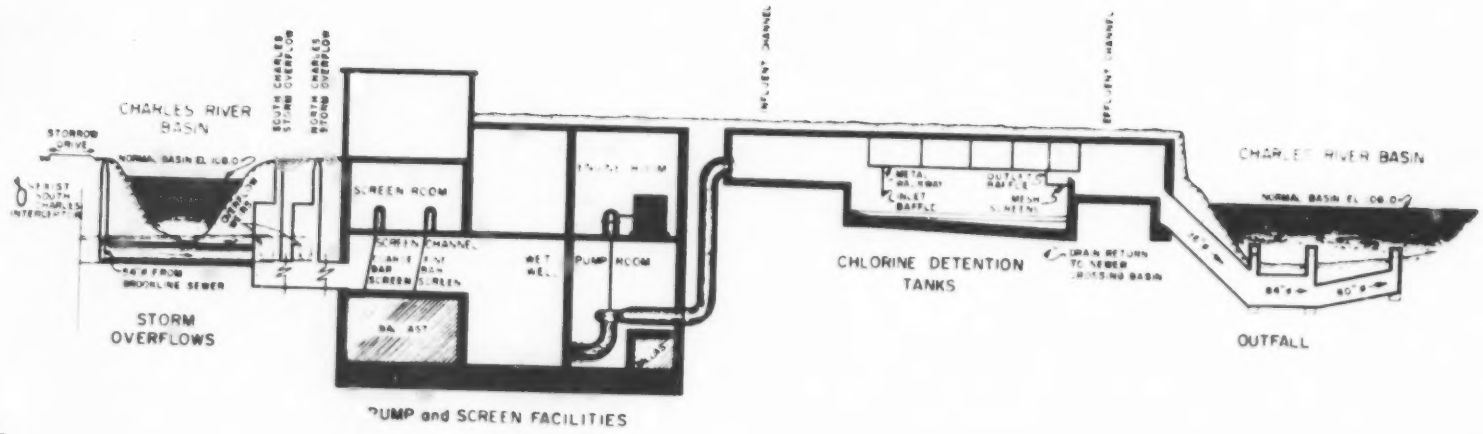


Figure 17. Boston's BU storm detention and chlorination station



OWNER

COMMONWEALTH OF MASSACHUSETTS — FRANCIS W. SARGENT, GOVERNOR
METROPOLITAN DISTRICT COMMISSION — JOHN W. SEARS COMMISSIONER
ASSOCIATE COMMISSIONERS: J.F. HAGGERTY, A.T. LYMAN JR., V.P. O'BRIEN, M. ROSENBLATT

CONTRACTOR

DE MATTEO CONSTRUCTION COMPANY

ENGINEER

CHARLES A. MAGUIRE & ASSOCIATES, INC.

LOCATION

NEAR BOSTON UNIVERSITY BRIDGE

CAPACITY

233 MILLION GALLONS PER DAY

Figure 18. Boston's BU storm detention and chlorination station, flow diagram

SHUTDOWN

If it should become necessary to shut down the instrument, as might be the case through a long winter when storm flows might be moderated by long freezing conditions, the instrumentation should be operated on water continuously for a period of at least an hour. During this interval, lines will be flushed and samples purged from the delivery system to eliminate settling and coagulation that could be expected to plug the system on start-up. Start-up after a prolonged shutdown should be programmed to follow an inspection and maintenance routine.

ENGINEERING MODEL DATA

Components were selected for the design and assembly of an instrument for the reliable measurement of Total Organic Carbon (see Figure 13). Data (see Table 11) were collected in Raytheon's TOC development laboratory. After the instrument was found to give a satisfactory determination of Total Organic Carbon concentration, the instrument was moved to the municipal wastewater treatment plant at Cranston, Rhode Island (Figure 19) where it was tested continuously in unattended operation with raw sewage for a period of several weeks.

In the above tests we have shown that sample handling, oxidation reactor and hardware assembly are well designed for the purpose of monitoring Total Organic Carbon, TOC. Early problems with signal noise have been reduced substantially by processing the sample with continuous blending through Raytheon's blender (Figure 9). The response time of the present instrumentation is less than five minutes when going from a signal that is indicating 600 mg/l of carbon present as cyclohexanol to water and then back to sewage. This is seen in Figure 20.

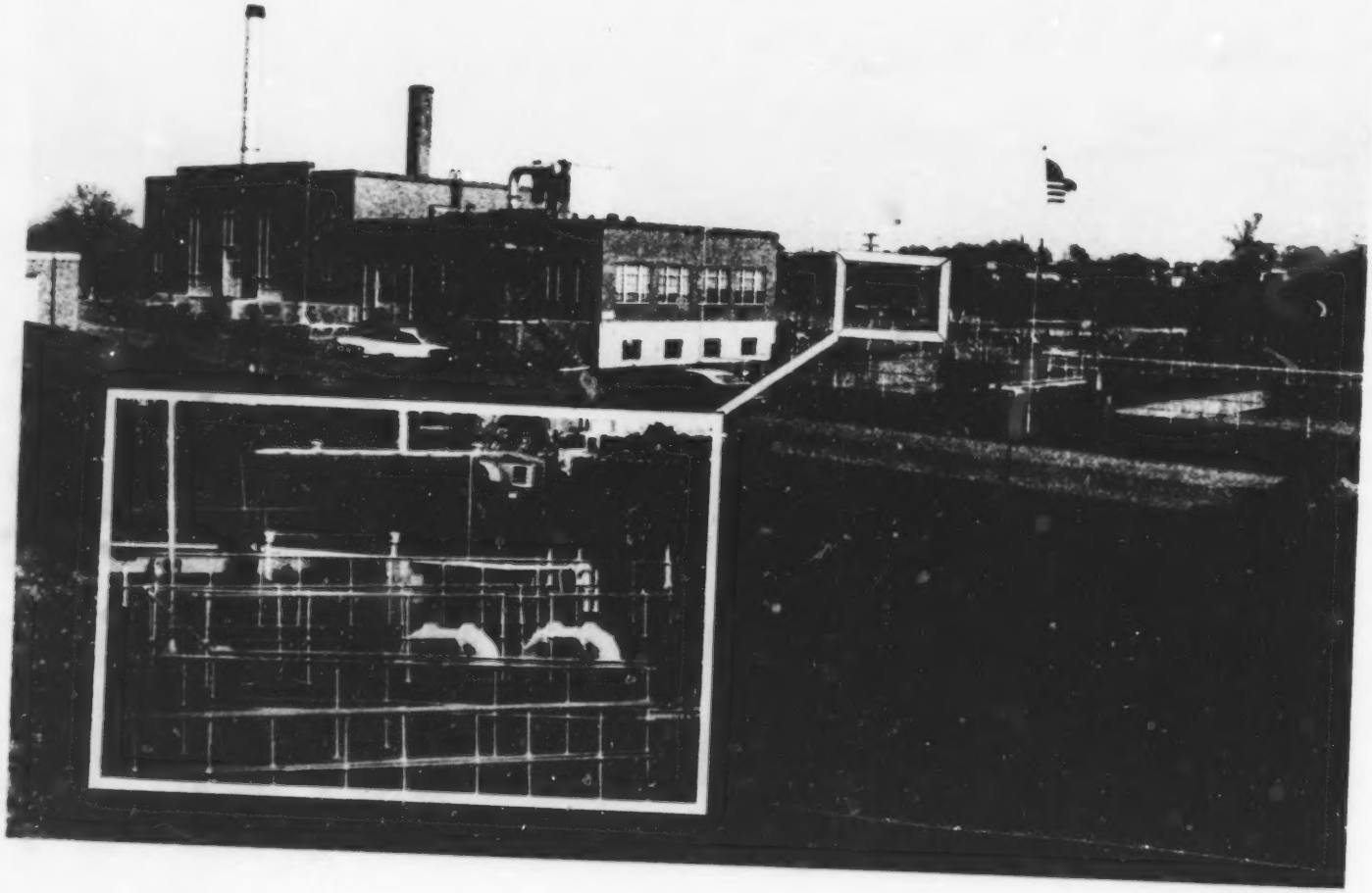


Figure 19. Municipal wastewater treatment plant, Cranston, RI (sheet 1 of 3)

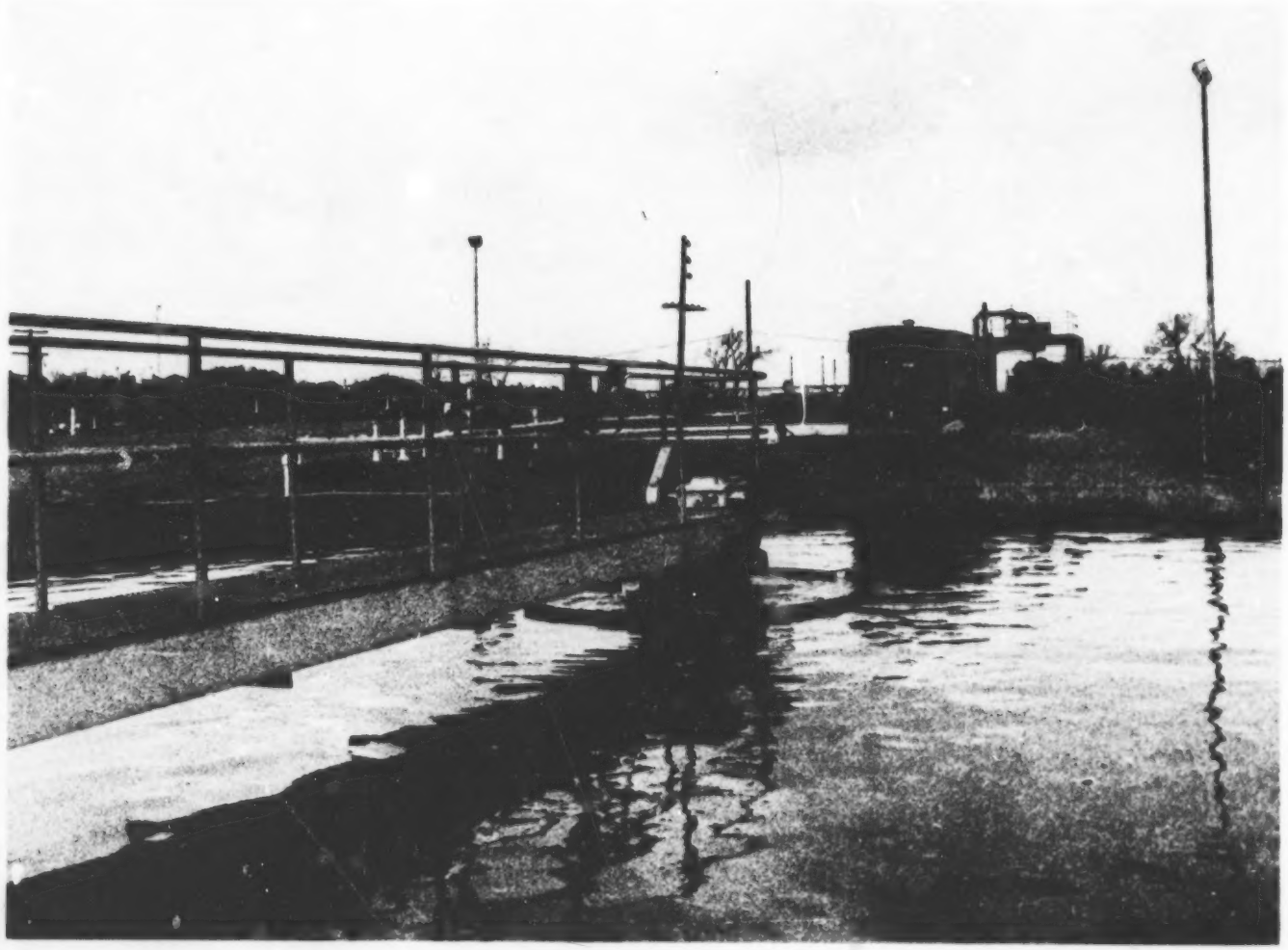


Figure 19. Municipal wastewater treatment plant, Cranston, RI (sheet 2 of 3)

Figure 19. Municipal wastewater treatment plant, Cranston, RI (sheet 3 of 3)

Table 11. DATA SHEET FOR CHARACTERIZATION OF SEWAGE AND CORRELATION WITH TOC ANALYSIS

	1ST DAY												2ND DAY												MEAN		SD	
	T1			T2			T3			T4			T1			T2			T3			T4						
PROPOSED TOC																												
	TC	TIC	TOC	TC	TIC	TOC	TC	TIC	TOC	TC	TIC	TOC	TC	TIC	TOC	TC	TIC	TOC	TC	TIC	TOC	TC	TIC	TOC				
REPLICATES BECKMAN TOC 1																												
REPLICATES BECKMAN TOC 2																												
REPLICATES BECKMAN TOC 3																												
REPLICATES BECKMAN TOC 4																												
REPLICATES BECKMAN TOC 5																												
MEAN																												
STAND. DIV.																												
TOC SOLUBLE																												
SETTLEABLE SOLIDS																												
SUSPENDED SOLIDS																												
VOLATILE SUSPENDED SOLIDS																												
TOTAL DISSOLVED SOLIDS																												
MICROSCOPIC EXAMINATION																												

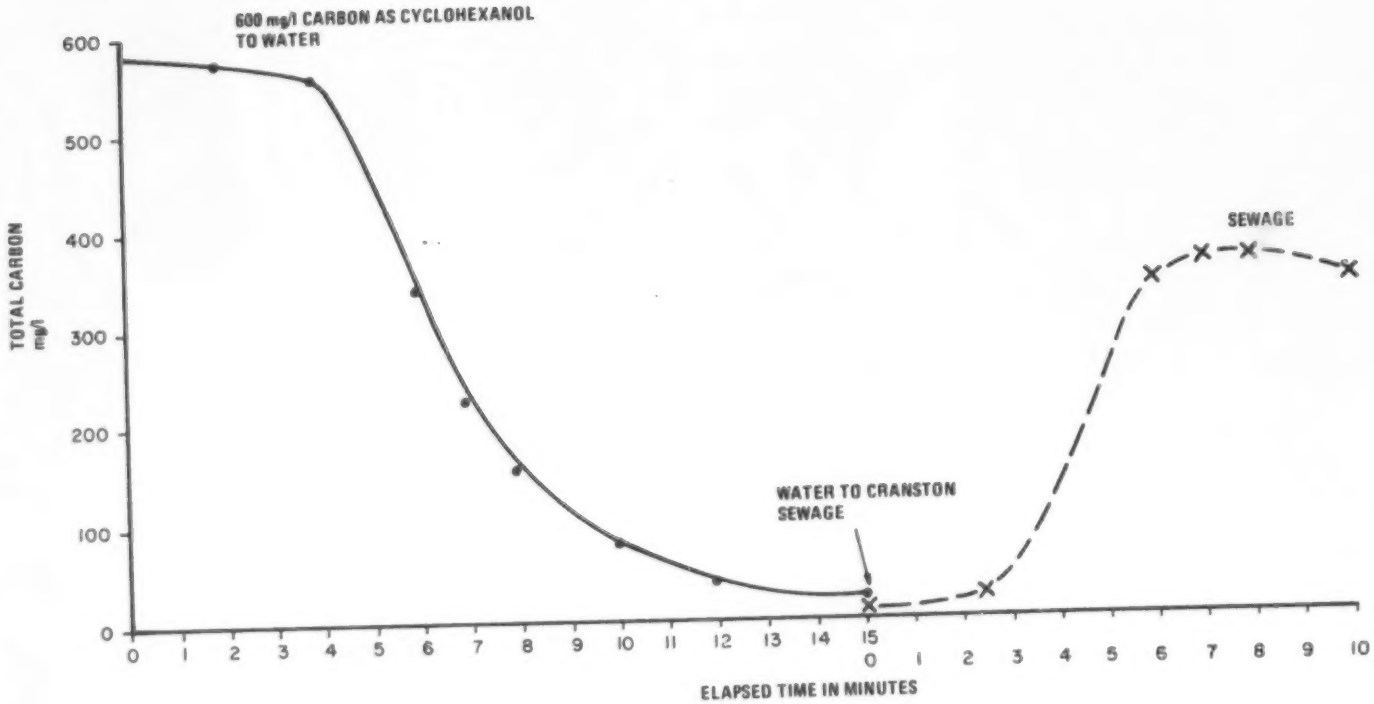


Figure 20. Response time of organic cyclohexanol solution to water and .o sewage

FUTURE ACTIVITIES

Our immediate effort will be to operate the present design continuously and without attention on the ground, blended and flowing raw sewage at the Cranston plant. Instrumentation associated with municipal sewage has been plagued by assembly failures, breakdowns and unreliable performance. With this background, it is essential that data be obtained with a view toward establishing a sense of confidence in the assembly and its design. The forthcoming laboratory evaluation program provides the opportunity to document the following important instrumentation parameters:

- Accuracy
- Repeatability
- Long-Term Drift
- Signal-to-Noise Ratio
- Sensitivity
- Correlation of the above with Sewer System Characteristics of
  - TOC Soluble
  - Settleable Solids
  - Suspended Solids
  - Volatile Suspended Solids
  - Total Dissolved Solids
  - Microscopic Examination.

In order to obtain information on the instrumentation parameters listed above, Raytheon's staff has designed the experiment in Table 11.

Once the technology has been established for the above characterization, samples will be obtained from MDC-BU for the characterization of stormwater during

the storm event. With the information obtained from these data we will be in a position to design instrumentation for monitoring stormwater TOC.

Because combined sewage is somewhat similar to dry weather raw sewage, the immediate objective of our program is to obtain information on the reliability and reproducibility of prototype TOC instrument on the samples obtained from the grit chamber of the primary settling basin at Cranston. Conducting our experiments at this facility will insure a "fresh" supply of samples that contain similar suspended solids.

In order to do this, it is necessary that stationary sample be delivered to the instrument so that a constant sample concentration can be drawn into the Total Organic Carbon analyzer. The sample will then be stabilized by bringing the sewage to a pH$<$2 so that samples are continuously analyzed over a period of time from the same stabilized, mixed reservoir. Results of this effort will provide an estimate of instrument variation over the period of time (drift) and the reliability of the proposed TOC instrument. During this phase, hand-conditioned (homogenized) samples analyzed with sufficient number of repetitions will serve as the primary standard. Table 11 shows a sample data form that will be used in accumulating the laboratory data.

As has been mentioned previously, the reason for assembling the data in Table 11 is to determine the precision of the instrument in making the measurement of interest. This may also be described as repeatability. The reason for running the same sample for two days is to obtain an estimate of the long-term drift of the measurement. These tests and several others to be described later may be used to give a sense of the accuracy of the instrument.

Accuracy is the ability of a system to approximate a true value. In general, accuracy is estimated. For our purposes, the standards of quantitative analysis

should be a suitable method of standardizing our equipment. Potassium acid pthalate, when properly handled, is a standard of material from which a solution of known organic carbon composition can be prepared. There is a considerable history of application of this material in quantitative analysis. Solutions could be standardized by titration with sodium hydroxide. This procedure will demonstrate the ability of an instrument to measure Total Organic Carbon in a solution of known composition, or serve as a method of calibration.

There is a large problem in solutions of unknown compositions containing some carbon as suspended solids. For some compounds (e.g., anthrocite), residence time in the reactor might be too short to give complete combustion. For similar compounds it may be impossible to grind them to a particle size sufficient to pass through a syringe in the Beckman even though the residence time might be essentially infinite. One would expect distortion of the Beckman signal where combustion residence time is variable. In the case of incomplete combustion, the mean TOC value obtained from the Beckman should be higher than that from the proposed TOC. If the solid sample cannot be passed through a syringe, the Beckman should produce a lower mean value than the proposed TOC analyzer.

Observations of this kind will make it possible to discuss the accuracy of the instrument.

Since the ultimate objective of this program is to design a device for the automatic, rapid on-site monitoring of the organic loading of storm and combined sewer flows, some additional modification of the prototype instrument is necessary for unattended operation in storm conditions.

Several features remain to be automated in the design of a stormwater TOC. The start-up and shut-down operation will require automated signaling as a result of certain occurrences such as storm events or sewer flooding.

The present design which incorporates O_2 as the reactive gas should be adapted for use with CO_2 free air. This will require some modification of the present design.

SECTION XI

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